Process Parameters for Successful Synthesis of Carbon Nanotubes by Chemical Vapor Deposition: Implications for Chemical Mechanisms and Life-cycle Assessment

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Thesis submitted in partial fulfillment of
the requirements for the degree of
Master of Science in the Department of
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ABSTRACT

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Abstract

Manufacturing of carbon nanotubes (CNTs) via chemical vapor deposition (CVD) calls for thermal treatment associated with gas-phase rearrangement and catalyst deposition to achieve high cost efficiency and limited influence on environmental impact. Taking advantage of higher degree of structure control and economical efficiency, catalytic chemical vapor deposition (CCVD) has currently become the most prevailing synthesis approach for the synthesis of large-scale pure CNTs in past years. Because the synthesis process of CNTs dominates the potential ecotoxic impacts, materials consumption, energy consumption and greenhouse gas emissions should be further limited to efficiently reduce life cycle ecotoxicity of carbon naotubes. However, efforts to reduce energy and material requirements in synthesis of CNTs by CCVD are hindered by a lack of mechanistic understanding. In this thesis, the effect of operating parameters, especially the temperature, carbon source concentration, and residence time on the synthesis were studied to improve the production efficiency in a different angle. Thus, implications on the choice of operating parameters could be provided to help the synthesis of carbon nanotubes.

Here, we investigated the typical operating parameters in conditions that have yielded successful CNT production in the published academic literature of over seventy articles. The data were filtered by quality of the resultant product and deemed either "successful" or "unsuccessful" according to the authors. Furthermore, growth rate data

were tabulated and used as performance metric for the process whenever possible. The data provided us an opportunity to prompt possible and common methods for practioners in the synthesis of CNTs and motivate routes to achieve energy and material minimization.

The statistical analysis revealed that methane and ethylene often rely on thermal conversion process to form direct carbon precursor; further, methane and ethylene could not be the direct CNT precursors by themselves. Acetylene does not show an additional energy demand or thermal conversion in the synthesis, and it could be the direct CNT precursors by itself; or at least, it would be most easily to get access to carbon nanotube growth while minimizing synthesis temperature. In detail, methane employs more energy demand (T_{avg}=883℃)than ethylene (T_{avg}=766℃), which in turn demands more energy than acetylene (T_{avg}=710℃) to successfully synthesize carbon nanotubes. The distinction in energy demand could be the result of kinetic energy requirements by the thermal conversion process of methane and ethylene to form direct CNT precursors, and methane employs the highest activation demand among three hydrocarbons. Thus, these results support the hypothesis that methane and ethylene could be thermally converted to form acetylene before CNT incorporation.

In addition, methane and ethylene show the demand for hydrogen in thermal conversion process before CNT incorporation; whereas, hydrogen does not contribute to the synthesis via acetylene before CNT incorporation, except the reduction of catalyst.

At relatively low hydrogen concentration, this work suggests that hydrogen prompts growth of carbon nanotubes via methane and ethylene, probably by reducing the catalysts or participating thermal reactions. In addition, "polymerization-like formation mechanism" could be supported by the higher growth rate of CNTs via ethylene than acetylene.

There could be an optimum residence time to maintain a relatively higher growth rate. At too low residence time, carbon source could not be accumulated, causing a waste of material; while too high residence time may cause the limitation of carbon source supplement and accumulation of byproducts.

At last, high concentration of carbon source and hydrogen could cause more energy consumption, while it helps to achieve a high growth rate, due to the more presence of direct carbon precursor.

Dedication

To my parents, Quanfu and Lan, for always standing by me

To my advisor, Dr. Desiree Plata, for the selfless help

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List of Abbreviations

CNTs: Carbon Nanotubes

CCVD: Catalytic Chemical Vapor Deposition

SWCNTs: Single-walled Nanotubes

MWCNTs: Multi-walled nanotubes

CVD: Chemical Vapor Deposition

GSHC: Gas–Solid Heterogeneous Catalysis

Acknowledgements

I would like to express the deepest appreciation to my committee chair, Professor Desiree L. Plata, who has the attitude and the substance of a genius: she continually and convincingly conveyed a spirit of adventure in regard to research, and an excitement in regard to teaching. Without her guidance and persistent help this thesis would not have been possible.

I would like to thank my committee members, Professor P. Lee Ferguson and Professor Mar Deshusses, whose work demonstrated to me that concern for quantitative analysis of parameters in low-temperature synthesis process of carbon nanotubes.

In addition, I really appreciate my parent's support, with which I have the opportunity to overcome difficulties and go beyond myself.

1. Background on the synthesis of CNTs by CCVD

1.1 Introduction

In past years, a large number of nanomaterials have become hot topics. Carbon nanotubes (CNTs) are particularly attractive among them, due to their unique properties on structure and performance; however, CNT production is still among the most energetically expensive manufacturing processes of all materials [167]. Therefore, large-scale industrial application of carbon nanotubes imminently calls for cost efficiency, commonly achieved by low-temperature synthesis and less material consumption [168]. Further, the high temperature processing and low synthetic yields lead to toxic byproduct and greenhouse gas emission many orders of magnitude higher than the mass of product itself [169]. Thus, manufacturing of CNTs could dominate their environmental impact [170]. In this way, the synthesis process of CNTs has become a research hot spot and drawn widespread attention.

CNTs , which are allotropes of carbon, have been constructed in a cylindrical nanostructure with a extremely large length-to-diameter ratio of up to 132,000,000:1[1]. Nanotubes can be categorized as single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs). SWCNTs can be thought of as grapheme wrapped into a cylindrical structure at specific chiral angles, while MWCNTs are comprised of concentric graphitic cylinders. CNTs have good tensile strength [2] and elastic modulus,

resulting from the covalent sp^2 bonds formed between the individual carbon atoms. CNTs have unusual electrical properties that they can perform both metallic and semiconducting function, based on the numbers of unit vectors along two directions in the honeycomb crystal lattice of grapheme [3]. In addition, good thermal conductivity and optical properties make CNTs an important kind of novel nanomaterials as well. These unusual properties are so valuable for electronics, optics and other fields of materials science and technology that CNTs have been widely applied in electrical circuits [4], solar cells [5], hydrogen storage [6], improving experimental capacity [7] and many other fields.

Since the first synthesized CNTs reported in 1950s [8, 9], synthesis method of CNTs has rapidly developed. In the early years, researches on CNTs just focused on microscopic and theoretical aspects [10], because lack of synthesis approaches provided less availability to get CNTs sample. Then some new approaches, such as arc-discharge and laser ablation, were developed to get access to a large quantity of pure CNTs samples. Taking advantage of economical efficiency, catalytic chemical vapor deposition (CCVD) has currently become the most prevailing synthesis approach for the synthesis of large-scale pure CNTs. As a standard process for the synthesis of CNTs, various aspects of CCVD process have been reached, such as growth mechanism [12-18], structure control of CNT production [19-24] and large-scale production, to achieve

progress on synthesis yield, nanotube alignment and sample purity [11]. However, the CNTs production efficiency still attracts increasing attention to synthesize CNTs at lower temperature with higher yield to save energy and material consumption.

The environmental impacts of carbon nanotubes arise from both releases of carbon nanotubes and their production. However, ecotoxicity of carbon nanotubes production by CVD process exceeds that of releases in realistic by three orders of magnitude [170]. In production process, 93% of ecotoxicity is dominated by the synthesis [170]. At the same time, the great majority of life cycle ecotoxicity in CNT synthesis indirectly results from the emission of bioactive metals, largely from the combustion of fossil fuels for the generation of electricity used during CNT synthesis, or to produce various input chemicals, rather than direct CNT products [170]. In this way, materials consumption, energy consumption and greenhouse gas emissions should be further limited to efficiently reduce life cycle ecotoxicity of carbon naotubes.

In recent years, several approaches have been proposed to achieve low-temperature synthesis of CNTs. Mingwei Li et al. combined non-equilibrium plasma reaction with template-controlled growth technology to synthesize MWCNTs at a temperature lower than 200° C [175]. Synthesis with assistance of plasma has been widely applied; however, undesirable defects in the CNT structure could be generated due to etching by ionized species via plasma-enhanced methods [176, 177, 178]. In

addition, many kinds of oxygen-containing materials (e.g., acetone, carbon dioxide and water) have shown significant support function to decrease the reaction temperature by improving the lifetime of catalyst and growth rate of CNTs [179, 180]. Alternatively, transition-metal nanoparticles can work as catalyst for the synthesis of CNTs by promoting the decomposition process of hydrocarbon precursors at a lower temperature than that of spontaneous decomposition process [181]. Nevertheless, approaches could still be found to reduce synthesis temperature of CNTs, due to the limited knowledge on the growth mechanisms. Most research has been done on the catalyst to improve the efficiency, such as catalyst modification by pre-growth chemical activation [25–27] and prevention of catalyst poisoning, but few on the effect of operation parameters of the process at macroscopic level.

On the other hand, efforts to reduce energy and material requirements in synthesis of CNTs by CCVD are hindered by a lack of mechanistic understanding. The exact mechanism is unknown, because most syntheses are conducted in hot-wall reactors, where temperature simultaneously influences gas phase reactions, catalytic activity, and provides the energy required by the reactions.

Here, we sought to delineate the typical operating parameters that have yielded successful CNT production in the published academic literature of over seventy articles. These data encapsulate the landscape of possible and common methods that could be

used to industrially fabricate nanomaterials, and thus, could inform subsequent life cycle assessment as well as provide a useful tool for practioners. Further, the data delineated here can be used to highlight opportunities for energy and material minimization and shed light on the true energetic limitations in CNT synthesis.

1.2 Background on CCVD

1.2.1 Synthesis System

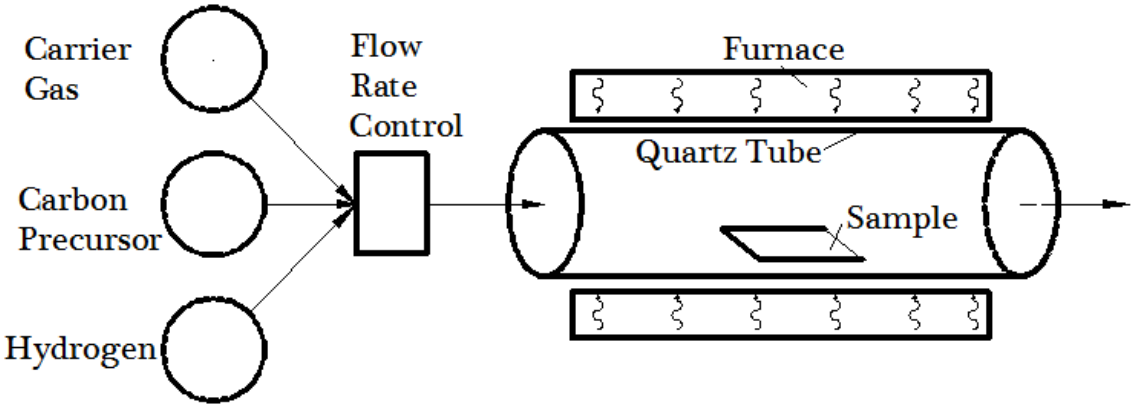


Figure 1: Schematic diagrams of apparatus for CCVD.

The key synthesis system of CCVD can be summarized as that catalytic transition metal nanoparticles deposited on specific substrate (e.g., SiO_2 and Al_2O_3) is heated at high temperature (500-1100° C) in the presence of carbon precursor, referring to gaseous carbon-containing molecules. Inert gas (e.g., Ar, N_2 and He) is firstly introduced to the reactor (quartz tube) to remove the air in the reactor; meanwhile, the catalytic transition metal nanoparticles associated with the reactor (hot-wall reactor) are heated

by tubular electric furnace to the temperature required for the synthesis (Fig. 1). Then carbon precursor, predominantly hydrocarbons (e.g., CH_4, C_2H_4 and C_2H_2) with hydrogen carried by inert gas, is introduced to the reactor. At the required temperature, carbon atoms, dissociated from gaseous carbon-containing molecules, diffuse through the catalytic nanoparticles (e.g., Fe, Ni and Co) and subsequently precipitate to be incorporated into tube wall. In addition, hydrogen, oxygen and some other oxygen-containing materials (e.g., H_2O and CO_2) [10, 28] have been reported to support the synthesis process, despite of the ill-understood influence.

1.2.2 Reactor Types

Hot wall reactor and cold wall reactor are most frequently used in CCVD process.

1.2.2.1 Hot Wall Reactor

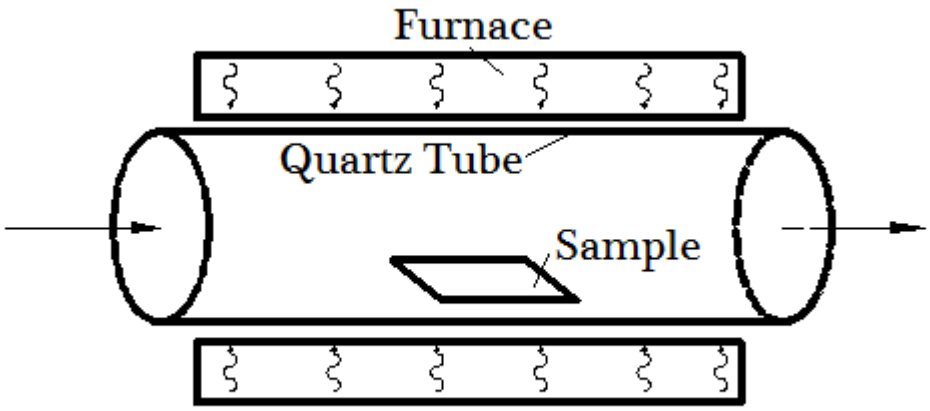


Figure 2: Schematic diagrams of hot wall reactor.

In hot wall reactor (Fig. 2), the environment in the reactor, especially the gaseous carbon precursor, catalyst and reactor wall, has the same temperature, due to that the reactor is enwrapped by the tube furnace. Thus, plenty of catalyst could be placed in the reactor. However, high temperature of the wall may cause undesirable deposition to contaminate the synthesis process.

1.2.2.2 Cold Wall Reactor

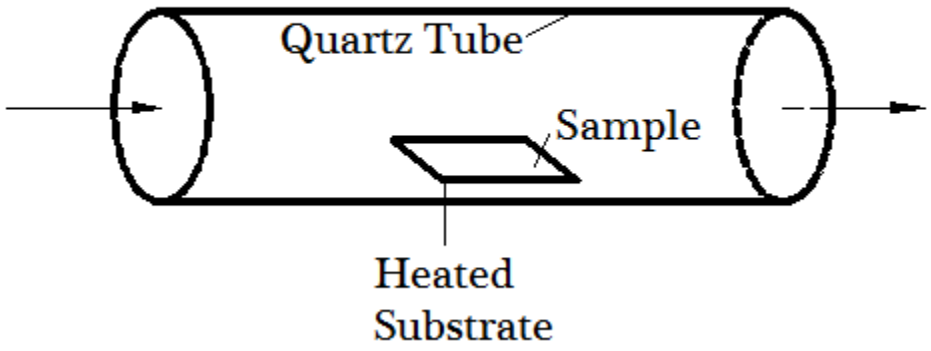


Figure 3: Schematic diagrams of cold wall reactor.

In cold wall reactor (Fig. 3), only heated substrate, where the catalyst placed, is heated. In this reactor, undesirable deposition can be avoided.

1.2.3 Related Factors

1.2.3.1 Carbon Source

As a flexible method, both volatile solid-phase (e.g., camphor, naphthalene and ferrocence) [29] and liquid-phase hydrocarbons (e.g., benzene [30] and alcohols [31]) can be used as carbon source for the synthesis of CNTs by CCVD, while gas-phase hydrocarbons (e.g., methane, ethylene and acetylene) [10] are most frequently used. The formation of CNT precursors, which are directly used into CNT incorporation, using different carbon source, requires different synthesis temperature. However, it may simply be an experimental artifact rather than a true difference in growth mechanisms

[174]. In the reactions of methane, ethylene and acetylene, hydrogen is generated and promotes the synthesis process [11], by reducing the catalysts to maintain the high activity and controlling the decomposition velocity [58], and influence the formation of CNT precursors. In addition, water vapor has been proved to be a kind of assistance material for the synthesis to improve the efficiency by improving lifetime of catalyst and growth rate of CNTs, because water can function as weak acid to selectively remove amorphous carbon [29, 32]. The reaction between acetylene and carbon dioxide can efficiently decrease the temperature required by the synthesis to even below 400° C [33]. Many kinds of oxygen-containing materials (e.g., acetone, ethanol and methyl-benzoate) have shown support function to decrease the reaction temperature [10].

1.2.3.2 Catalyst

Generally, transition-metal nanoparticles work as catalyst for the synthesis of CNTs by promoting the decomposition process of hydrocarbon precursors at a lower temperature than that of spontaneous decomposition process [29]. Among the transition metal nanoparticles, Fe, Ni and Co, are the most frequently used catalysts, due to the high solubility and high diffusion rate [29] for carbon atoms at high temperature. The high melting point and low equilibrium vapor pressure of these metals also provide a widely suitable temperature range for a large number of hydrocarbons [29].

Apart from Fe, Ni and Co, many other kinds of metal have been demonstrated to be

effective catalysts, such as Pd [34], Pt [34], Au [34], Mn [34], W [34], Ti [34], TiC [35], Mg [34], Al [34], In [34], Na [34], K [34] and Cs [34] for synthesis of MWCNTs. In the synthesis of SWCNTs, other transition metals (e.g., Pd [36], Pt [36] and Ru [37]) can be used as catalyst; besides transition metals, numerous metals also shows catalysis, such as noble metals (Cu [36,38], Ag [36], Au [36,39]), early transition metals (Mn [40], Cr [41], Mo [42]), elements of the carbon family (diamond [43], Si [44], Ge [44], Sn [41], Pb [41]), lanthanides (Gd [45], Eu [45]) and other mixed compounds ($FeSi_2$ [46], SiC [44,47], SiO_2 [48,49], Al_2O_3 [49], TiO_2 [49], Er_2O_3 [49], ZnO [50]) [11].

The mixture of active catalysts, which contains two kinds of active metals or the mixture of an active metal and co-catalytic weak- active metal (e.g., Mo [51,52] and Mg [53]), are also frequently used in the synthesis [11].

1.2.3.3 Other Factors

Generally, CNTs can be synthesized in a wide temperature range of 500-1100 ℃, in which the increasing temperature dramatically increases the diameter and diameter distribution of the CNTs in some cases[29]. In addition, MWCNTs are in dominant position at low-temperature (500-850 ℃), while SWCNTs begin to succeed the majority at high temperature.

The catalytic activity of catalyst is closely related to the kind of substrate; because same catalyst may has different catalytic activities when deposited on different

substrates. Different chemical bonds may be formed between catalyst and substrate, based on the interaction between them. In general, quartz, silica and alumina are the frequent used substrate [29].

1.3 Important Hypotheses on Growth Mechanisms

Although many debatable questions about growth mechanism are still investigated, generally speaking, three main processes primarily give rise to the synthesis of CNTs: (1) catalytic reactions of hydrocarbons to direct CNT precursors, (2) diffusion of direct CNT precursors through the catalyst nanoparticles, (3) incorporation of carbon atoms into CNTs [54-57].

1.3.1 Thermal Conversion of Hydrocarbons

The temperature required by decomposition of hydrocarbon depends on the types of catalyst and hydrocarbon [57], by which the chemical reactions are determined. As an independent process, the temperature required by incorporation is not closely related to the types of hydrocarbon, resulting in a poorly known stage. However, low-temperature synthesis was mostly obtained by using hydrocarbons with exothermic decomposition (e.g., C_2H_4 and C_2H_2) [57]. Thus, the threshold temperature of decomposition may determine the overall temperature of the synthesis process (i.e., synthesis of CNTs by CCVD at low-temperature is a hydrocarbon decomposition limited growth [57]).

1.3.2 Mechanisms of Carbon nanotube Formation

In early years, a vapor-liquid-solid (VLS) mechanism was used to explain the formation of carbon nanotubes. It was reported that high temperature in the synthesis system results in the formation of liquid or solid molten metal droplets which act as catalyst and scission of C-C bond in hydrocarbon to form C_2 unit, carbon atom and C-H fragments [182]. The carbon units further dissolve in the liquid or solid droplets, and cause the droplets to become oversaturated. Subsequently, the catalytic nanoparticles work as the medium to transport dissolved carbon units from the vapor to the tips of carbon nanotubes by diffusion. Then carbon nanotubes can be incorporated by precipitation on the tips of carbon nanotubes and dehydrogenation in the catalysts [182]. In addition, CNTs can only grow in the areas activated by the catalytic nanoparticals to determine the size and position of CNTs. Here, the VLS theory was supported by experimental observations.

On the other hand, a polymerization-like formation mechanism has been proposed to lead the CNTs growth [174], when alkynes are present as carbon feedstock (Fig. 4(a)). Metal catalysts require to be reduced to remain the catalytic activity, resulting from that electrons helps the bond formation. Thus, hydrogen, the most commonly used reducing gas, are always required to reduce the metal prior to CNT growth. At low partial pressures of hydrogen (Fig. 4(b)), the catalytic life time would sharply decrease,

because less hydrogen could re-reduce the catalyst after the hydrogen has been oxidized. However, high partial pressures of hydrogen would terminate chain propagation by blocking monomer addition [174] (Fig. 4(c)).

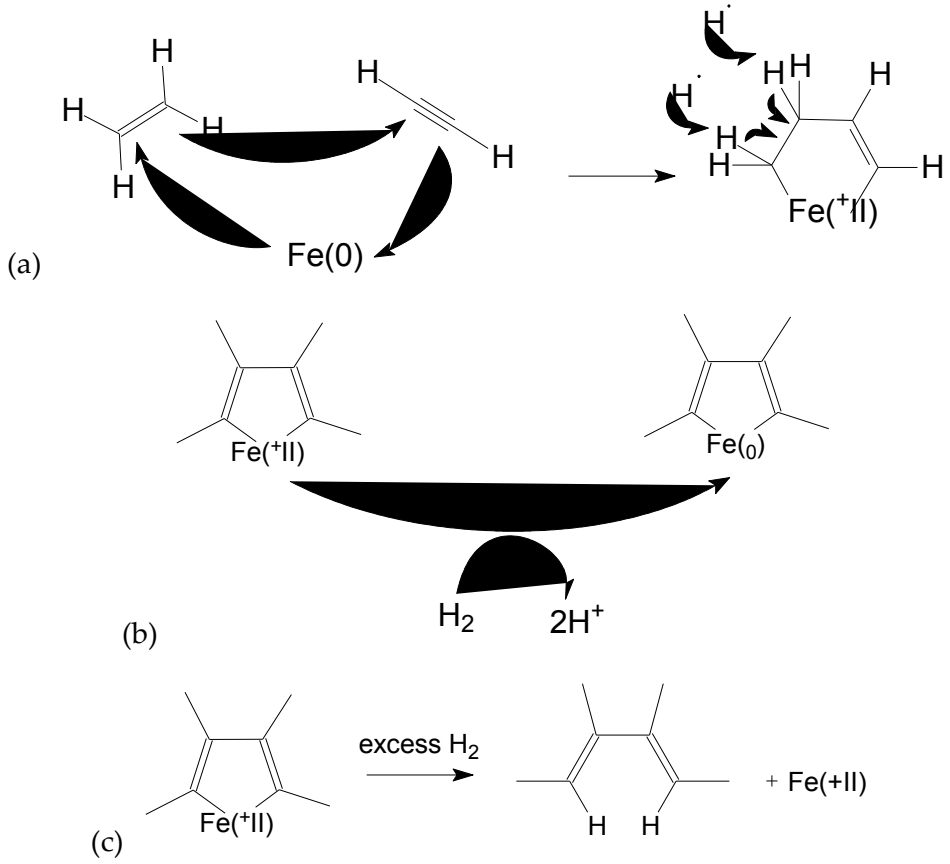


Figure 4: (a) Chemical effects of ethylene and hydrogen during acetylene-assisted CNT growth; (b) Low partial pressures of hydrogen reduce the catalyst to increase catalytic lifetime; (c) High partial pressures of hydrogen terminate "chain" propagation [174].

1.3.3 Diffusion Mode on Catalytic Agent

The driving force of diffusion takes the central stage of growth mechanism; leading to two most commonly accepted mechanisms. The first one implies that

temperature gradient across the catalytic nanoparticles acts as the driving force for the diffusion of carbon atoms through the catalytic nonaparticles, resulting from an exothermic decomposition of the hydrocarbon on the surface of the metallic catalyst nanoparticles and the endothermic deposition of carbon atoms on the opposite surface of the nanoparticles [59, 62].

Apart from driving force for diffusion, another key of contention focus on whether the diffusion of carbon through metal nanoparticles is surface diffusion or bulk (volumetric) diffusion [29]. In 2004, nickel cluster was reported to remain crystalline with well-faceted shapes, and graphite layer grown by a dynamic interaction between carbon and nickel atoms, resulting to changing nanocluster shape from spherical to cylindrical to align the grapheme layers around them. It illustrated that cluster boundary has effect on anchoring carbon atoms and weaving the graphene network, so that the carbon diffusion is a surface diffusion [29, 66]. On the other hand, an observation was reported that carbon atoms from the sidewalls got injected into the metal bulk and emerged in the form of new SWCNTs and MWCNTs, revealing that the carbon diffusion is bulk diffusion [29, 67].

2. Methods

2.1 Goals

CVD synthesis process of carbon nanotubes dominates the life-cycle ecotoxicity, by the emission of bioactive metals, largely from the combustion of fossil fuels for the generation of electricity used during CNT synthesis, or to produce various input chemicals, rather than direct CNT products. Materials consumption, energy consumption and greenhouse gas emissions in the synthesis process should be limited to efficiently reduce life cycle ecotoxicity of carbon naotubes. However, early choices in operating parameters for the synthesis initially cause a waste of material and energy. Efforts to reduce energy and material requirements in synthesis of CNTs by CCVD are cramped by a lack of mechanistic understanding.

Here, we summarized and analyzed the typical operating parameters that have yielded successful CNT production in the published academic literature of over seventy articles.

These data encapsulate the landscape of possible and common methods that could be used to industrially fabricate nanomaterials, and thus, could inform subsequent life cycle assessment as well as provide a useful tool for practioners. Further, the data delineated here can be used to highlight opportunities for energy and material minimization and shed light on the true energetic limitations in CNT synthesis.

2.2 Data Collection

The data were collected from over seventy published papers, in which CNTs have been successfully synthesized. These papers were published by the reputable scholars, who were practiced in the synthesis of carbon nanotubes by CVD. The data showed the available conditions for the synthesis of CNTs, as well as the unsuccessful conditions. These manuscripts were found via Duke Library search engine and Google Scholarship, with the following keywords: low-temperature synthesis of CNTs, synthesis of CNTs, carbon nanotubes, carbon nanotubes chemical vapor deposition, carbon nanotube growth, growth of carbon nanotubes, CVD growth carbon nanotubes, carbon nanotubes CCVD, CVD synthesis of carbon nanotubes.

We selected experimental approaches with cylindrical hot wall reactors and the hydrocarbon starting materials (i.e. methane, ethylene, and acetylene), which are among the most commonly used carbon sources in high-volume CNT synthesis. (Carbon monoxide is also employed in select high-volume production routes (e.g., SWeNT and the HiPCO processes), but was not interrogated in this investigation). The experiments only employed hydrogen and inert gases (i.e., N_2, Ar, He), and "general catalysts", including Fe, Ni, Co, Mo, Al, Cu, and mixture of them. The tabulated data included: (a) type of carbon source, (b) diameter of the reactor, (c) heated length of the reactor when specified (and otherwise assumed to be 30.48 cm, the length of the heated zone in the Lindberg Blue 1" to 3" tube furnace, a commonly used model), (d) synthesis

temperature, and (e) flow rates of the hydrocarbon, hydrogen, and associated carrier gases; (f) terminal length of CNT; and (e) synthesis time. Note that hydrogen is often utilized, but is not required to achieve CNT synthesis. Inert gases (e.g., nitrogen, helium and argon) are always employed, and influence final precursor concentration and residence time in the heated zone of the reactor.

In this work, we define starting material and feedstock gas to be gases that are purchased and intentionally introduced into the reactor. Precursor species are gases that are directly incorporated into the CNTs and may be the starting materials themselves or thermal byproducts thereof. Successful experiments were defined as the experiments in which carbon nanotube products were clearly observed.

The result of data collection is shown as Table 8 and 9 in appendix A.

2.3 Data Calculation

The parameters were tabulated or calculated as follows: (1) synthesis temperature, T (℃); (2) total flow rate, Q_t (sccm), where we assume the total flow rate is equal to the sum of the carrier gas, hydrogen, and hydrocarbon starting material (i.e., that each influent gas was explicitly mentioned in the respective manuscripts); (3) hydrocarbon starting materials flow rate, Q_c (sccm); (4) hydrogen flow rate, Q_h (sccm); (5) carbon source concentration, C_c (mol/cm^3), calculated by the ideal gas law as: $C_c=n/V=P_c/RT$, where P is partial pressure of specific hydrocarbon, $P_c=Q_c/Q_t \times P_t$(= 1 atm); (6)hydrogen concentration (mol/cm^3), calculated by the ideal gas law as: $C_h=n/V=P_h/RT$,

where P is partial pressure of specific hydrocarbon, $P_h=Q_h/Q_t \times P_t$(= 1 atm); (7) hydrogen/carbon source concentration ratio, C_h/C_c; (8) growth rate of carbon nanotubes (um/min),where growth rates were calculated by the terminal length of CNTs (um) divided by the reaction time (min); (9) volume of the reactor, V (cm^3), where $V=\prod \times r^2 \times L$, where L (cm) is the length of the heated zone of the reactor; and (10) standard residence time of the feedstock mixture (min), which reflects the average time the gas spends in the reactor, defined as:

$$\theta_s=V/Q_t \quad (2.1)$$

Note, the residence time was calculated as the one in standard condition (i.e., 0℃， 1 bar).

The synthesis temperatures were collected from the temperatures with the highest carbon nanotubes produced height.

The result of calculation is shown as Table 10 and 11 in appendix B.

2.4 Analytic Procedure

In order to conduct the statistical analysis, the data was processed in the following way. First, each manuscript contained multiple experimental parameters. In some cases, critical variables were unavailable and had to be calculated assuming standard operating conditions. For example, if the heated length of the reactor was not reported, but the model of the furnace was reported, the manufacturer's standard parameters could be used to determine the heated zone length. Second, “successful

experiments" were defined as the experiments in which carbon nanotube products were clearly observed. In order to compare the successful experiments, growth rate was calculated as the dependent parameters to measure the quality of CNT production in experiments. Growth rates were not directly reported, but calculated as the terminal CNT length or height divided by the reported synthesis time.

Then, I needed to reduce dimension of variables and unify the standard parameters. Here, growth rate and success of experiments were comprehensive results from effects of entire five parameters (i.e., temperature, carbon/ hydrogen/ total flow rate, reactor volume); but we could only do three dimensional analysis (two independent parameters vs. one dependent parameters). What we really care about is the patterns between material and energy. So we need to set up parameters basically reflecting changes in materials and energy to eliminate diversity across experiments. If carbon feedstock and hydrogen flow rate are used to respectively indicate the amount of carbon feedstock hydrogen, the diversity in reactor volume, temperature, and total flow rate would be neglected. It cannot basically reflect the amount of carbon feedstock in reactor. That was why I directly calculated concentrations of carbon feedstock and hydrogen. In this way, this work could not simply start with a selection of parameters from original ones, but the ones which has been unified across the experiments. Four standard variables were chosen in order to make consistent comparisons across the experiments; these included temperature, carbon source concentration, hydrogen

concentration, and residence time. Within these variables, synthesis temperature indicates the amount of energy input, while hydrogen and carbon source concentration indicate material supply. Total flow rate was used to calculate residence time, which has implications for material usage, emissions, and potential time for reaction in the heat zone. In this way, the effects of each variable on growth rate were investigated associated with temperature to check the patterns of energy and materials.

Using these data, linear regressions between both dependent and independent variables were conducted. Intercepts and slopes where determined using a standard software package StatPlus(™) and were deemed significant when p-values were less than 0.05; otherwise, relationships were deemed insignificant. I recognize that it is unconventional to seek correlations between two independent parameters, and I make the following arguments for the exercise: (1) to provide a visual representation of the operating parameter space for life cycle analysts and nanotube fabrication practitioners and (2) to determine if that space is related in practice, even if not causally linked. The material concentration and temperature matched in the experiments could be restricted to what is kinetically favorable. In other words, some patterns may emerge in these literatures when they were investigated as a whole. They are still required to be checked by further experiments with single variable control. If such relationships are observed, this work would serve to motivate further experimentation in which a single parameter varied.

3. Results and Discussion

3.1 Effects of Temperature on Success Rate of Syntheses and Implications

The frequencies of successful and unsuccessful synthesis of carbon nanotubes via three kinds of carbon source at different temperatures are summarized in Fig.5 (a). Although a wide range of temperature was employed to synthesize carbon nanotubes, successful syntheses were achieved in relatively smaller ranges of temperature. In the synthesis via methane, carbon nonatubes were successfully grown in the range of 700-1000 ℃ with a mode of frequency at 900 ℃ and average successful temperature at 882℃. In the synthesis via ethylene, carbon nonatubes were successfully grown in the range of 700-900 ℃ with a mode of frequency at 750 ℃ and average successful temperature of 765℃. In the synthesis via acetylene, carbon nonatubes were successfully grown in the range of 600-750 ℃ with a mode of frequency at 700 ℃ and average successful temperature at 710 ℃.

In order to investigate the relation between temperature and synthesis experiments, synthesis temperatures were resampled with 100 ℃ bins to eliminate the randomness of sample size at different temperatures (Fig. 5(b)). According to Table 1, success rate of the synthesis in each temperature bin are different for the experiments respectively via these three kinds of carbon source. It probably indicates that

temperature has influences on the synthesis process via methane, ethylene and acetylene, due to the varied success rate over temperature.

At first, success rates of the experiment via three kinds of carbon source all respectively present an approximately normal distribution. It probably demonstrates the effect of synthesis temperature on the activity of catalyst. At too low a temperature, the catalytic metal atoms could be not mobile enough to aggregate together into particles to nucleate and grow carbon nanotubes. If the temperature is too high, catalytic metal atoms might become so mobile that the particles aggregate to a too large size to nucleate and grow carbon nanotubes; rather, these particles would simply overcoat with carbon [183]. Thus, an optimum temperature could be required to maintain the activity of catalyst.

In addition, in the synthesis via methane, the highest success rate is observed in the range of 850-950 ℃. The popular temperature in my data set for carbon nanotubes growth via methane appears to be approximately 900 ℃, because experimentalists were most inclined to do experiments at this temperature and achieved the highest success rate. Similarly, the popular temperatures in my data set for carbon nanotube growth via ethylene and acetylene are respectively 750 ℃ and 700 ℃.

In the comparison on the popular and average successful temperatures between the three kinds of carbon source, an interesting phenomenon has been discovered that both popular and average successful temperature of synthesis via methane are the

highest, while synthesis via acetylene employs the lowest temperature. The shift of popular and average temperature does not simply result from experimentalists' experimental design; rather, it is the optimization from abundant trials. In this way, the distinction in demand for thermal treatment by these carbon sources could reveal a different thermal conversion process before carbon nanotube growth. Here, the experiments via three kinds of carbon source were all catalyzed by commonly used catalysts, including Fe, Ni, Co, Mo, Al, Cu and their combinations; and the specificity of catalyst distribution was not observed on temperature and type of carbon source. In addition, the diffusion process of carbon precursor through catalyst nanoparticles just requires approximate room temperature to be accomplished and shows non-specificity on types of carbon source. Thus, the temperature required to maintain the activity of catalyst and drive diffusion process could not well explain the shift of optimum temperature for the synthesis; further, it may result from the different demand for thermal treatment by these hydrocarbons to go through reactions and form the intermediate product (direct carbon precursor), which is directly used in the formation of carbon nanotubes with assistance of catalyst.

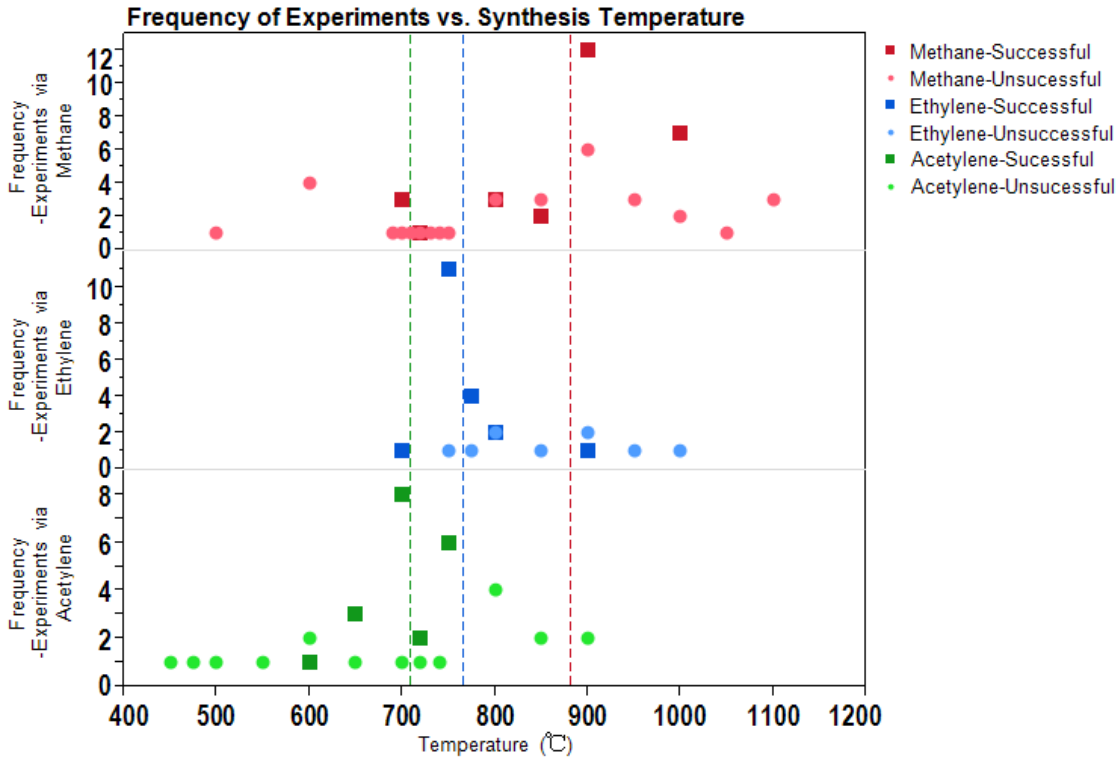
In a chemical reaction, some reactant molecules are with more energy than average energy level of primary state. When these molecules reach the energy state that high enough to go over the energy barrier, they become activated molecules to be available for the reaction. The reaction can only proceed after effective collision between

the activated molecules. As an energy-related parameter, synthesis temperature indicates the amount of energy input into the system. The highest popular temperature for the experiments via methane implies that methane demands for the most activation energy to initial overcome the energy barrier, while acetylene molecules require the least activation energy to overcome the activation energy. This could be better understood according to the molecule configuration of these hydrocarbons. Methane consists of four C-H σ -bonds with bond energy of 334 kJ/mol at 25 ℃.Ethylene consists of a C-C π -bond with bond energy of 272kJ/mol at 25 ℃, a C-C σ -bond and four C-H σ -bonds. Acetylene consists of two C-H σ -bonds, a C-C σ -bond, and two C-C π -bonds, the first one in which contributes 268 kJ/mol. Due to the less bond energy of C-C π -bond, less dissociation energy is required to break the C-C π -bond than to break C-C and C-Hσ -bonds, so that C-C π -bond is easier and inclined to be broken. In the reactions via methane, C-H σ -bond have to be broken with more dissociation energy; while in the reactions via ethylene and acetylene, C-C π -bond is preferred to be broken with less dissociation energy than C-C and C-Hσ -bonds. In this way, reactions via methane initially demand for the most activation energy, while acetylene initially demands for the least energy. At least, methane demands for the most energy to go through reactions before CNTs incorporation, and subsequently indicating the highest energy barrier employed by methane.

Thus, the distinction in popular and average temperature employed for these three carbon source to successfully synthesis carbon nanotubes could result from variety in kinetic energy demand.

At last, as discussed above, the successful synthesis temperature is the result of cooperation between activity of catalyst and kinetic energy demand in thermal conversion processes of carbon source. According to my data set, the thermal conversion processes of carbon source lead to the shift of popular temperature for these three kinds of carbon source. It suggests that the energy required by thermal conversion processes of carbon source could dominate the synthesis temperature.

(a)


Frequency of Experiments vs. Synthesis Temperature
Frequency -Experiments via Methane
Frequency -Experiments via Ethylene
Frequency -Experiments via Acetylene
Temperature (℃)
Methane-Successful
Methane-Unsucessful
Ethylene-Successful
Ethylene-Unsuccessful
Acetylene-Sucessful
Acetylene-Unsuccessful

(b)

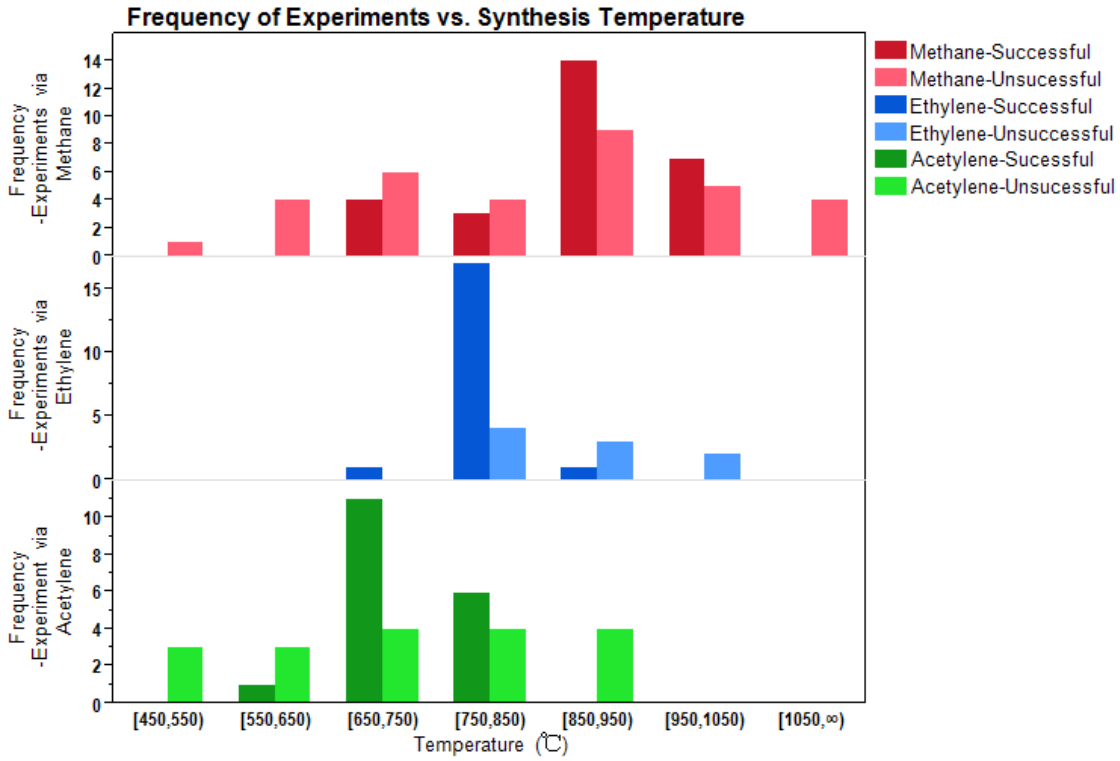


Figure 5: Frequency distribution of temperature (℃) for synthesis via three kinds of carbon source: (a) Initial samples of synthesis temperature; (b) histogram with 100 ℃ bins.

Table 1: Success rates of experiment in temperature groups with 100 ℃ bins.

	[450,550)	[550,650)	[650,750)	[750,850)	[850,950)	[950,1050)	[1050,∞)
Methane	0	0	40%	43%	61%	58%	0
Ethylene			100%	81%	25%	0	
Acetylene	0	25%	73%	60%	0		

3.2 Effects of Carbon Source Concentration associated with Temperature on Synthesis

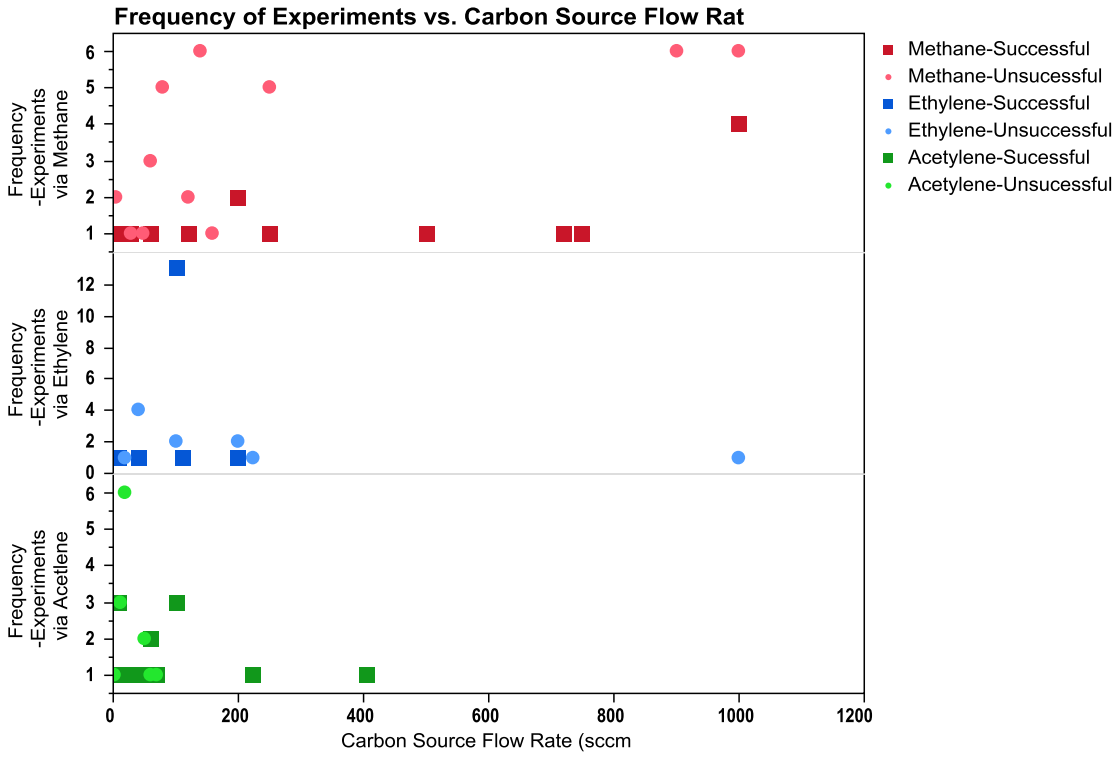
3.2.1 Effects of Carbon Source Flow Rate on Successful Rates of Synthesis

As shown in Fig. 6(a) and (b), the experiments via methane employed a wide range of carbon source flow rate in 0-1200 sccm, while ethylene and acetylene employed a relatively smaller range of 0-600 sccm. According to table 2, success rates of experiment respectively via methane, ethylene and acetylene vary over carbon source flow rate. In the statistics for success rate, an approximate normal distribution can be observed, and best success rate is respectively observed in the range of 400-800 sccm for methane, 0-200 sccm for ethylene, and 200-600 sccm for acetylene. However, the modes of the frequency for three carbon sources are all observed in a relatively low range of 0-200 sccm, and the ranges with best success rate do not have an adequate sample size. In this way, we could not directly derive scientific implications from the distribution; but at least, the distinction in success rate implies that carbon flow rate may have influence on the synthesis. Actually, the difference in carbon source flow rate substantively affects the concentration of carbon source in the reactor, and further provides us a possibility that the concentration of carbon source has influence on the synthesis. However, the reactor volumes, temperature, and total flow rate used in the experiments were not constant. A high carbon source flow rate cannot necessarily leads to a high concentration of carbon

source in the reactor, due to the variety of total flow rate, reactor volume, and temperature. Thus, carbon source concentrations of experiments via methane, ethylene and acetylene were directly calculated by ideal gas law to eliminate the difference of reactor volume and essentially reveal the amount of carbon source. Here, one thing needs to be pointed out that the calculated concentrations in this work represents the total concentration of the specific carbon source in the reactor without taking thermal conversion into consideration. In other words, it represents the "start concentration" without thermal conversion, and it differs from the concentration at equilibrium.

In addition, temperature has been implied to have effects on the synthesis by providing activation energy to prompt the reactions. As experimental parameters, temperature and carbon flow rate were set by experimentalists; however, the successful experiments could only be achieved, when energy and material were properly matched to make the reactions thermodynamically possible and kinetically favorable. Thus, the effect of carbon source concentration on the synthesis was investigated.

(a)


Frequency of Experiments vs. Carbon Source Flow Rat
Frequency -Experiments via Methane
Frequency -Experiments via Ethylene
Frequency -Experiments via Acetlene
Carbon Source Flow Rate (sccm
Methane-Successful
Methane-Unsucessful
Ethylene-Successful
Ethylene-Unsuccessful
Acetylene-Sucessful
Acetylene-Unsucessful

(b)

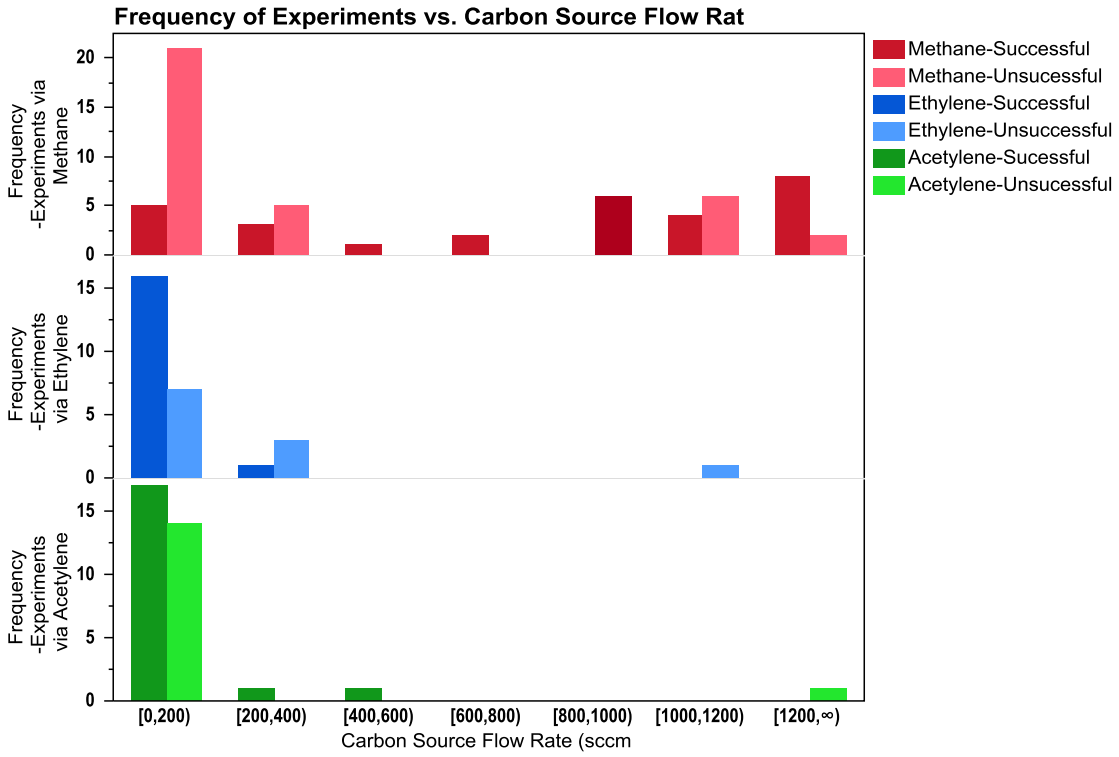


Figure 6: Frequency distribution of carbon source flow rate (sccm) for synthesis via three kinds of carbon source: (a) Initial samples of carbon source flow rate (sccm); (b) histogram with 200 sccm bins.

Table 2: Success rates of experiment in carbon source flow rate groups with 200 sccm bins.

	[0，200)	[200,400)	[400,600)	[600,800)	[800,1000)	[1000,1200)	[1200,∞）
Methane	19%	38%	100%	100%	0	40%	80%
Ethylene	70%	25%				0	
Acetylene	55%	100%	100%				0

3.2.2 Correlation Analysis between Carbon Source Concentration and Temperature for Successful Syntheses

Fig. 7 summarizes the carbon source concentrations and correspondent temperature for each successful and unsuccessful synthesis respectively via methane, ethylene and acetylene. The figure is employed to investigate whether interaction exists between carbon source concentration and temperature to make synthesis succeed, in addition to the previous discussions that carbon source concentration and temperature respectively have influences on the success of synthesis.

Linear regression was chosen as the model and respectively conducted for the successful syntheses via methane, ethylene and acetylene, according to the observation on scatter plot. As shown in table 3, the p-value of the slope tests the null hypothesis that the coefficient is equal to zero (no effect). A low p-value (< 0.05) indicates that the null hypothesis is rejected and the linear correlation between carbon source concentration and temperature is significant to get successful synthesis. In other words, a carbon source concentration that has a low p-value is likely to be a meaningful addition to the model, because changes in the value of carbon source concentration are correlated to changes in the temperature. Conversely, a larger (insignificant) p-value suggests that changes in the carbon source concentration are not associated with changes in the temperature. Here, concentrations of methane and ethylene have a low p-value (< 0.05), referring to that linear interaction is significant between carbon source

concentration and temperature employed in the successful experiments; however, acetylene concentration is not correlated to the temperature to make the synthesis successful.

Table 3 also shows the R-square values for the linear regressions of experiments via three kind of carbon source. R-square value is a statistical measure of how close the data are to the fitted regression line, and the percentage of the response variable variation that is explained by a linear model. As shown in table 3, R-square value of regression lines for experiments via acetylene is zero, indicating that linear model cannot fit the data of acetylene at all. The null R-square value of acetylene is consistent with the extremely high P-value. Thus, linear interaction does not exist between acetylene concentration and temperature. In addition, R-square value of methane and ethylene are not high enough. However, a regression with low R-square value is not inherently bad for a model, because R-square value does not indicate whether a regression model is adequate. We could have a low R-square value for a good model, or a high R-square value for a model that does not fit the data. On the other hand, the values of parameter may be influenced by human behavior, which is harder to predict than an entirely physical process, as the values were chosen by experimentalists in this research. For instance, if experiments were conducted respectively at 700℃, 725℃ and 750℃ associated with a specific carbon source concentration by a research group, among which the synthesis succeeded at 725 ℃, then 725 ℃ will be reported in the published

paper. However, 718℃ is the real optimum temperature, which should be observed at this specific value of carbon source concentration, assuming that carbon source concentration and temperature are indeed correlated to make synthesis succeed. In this case, a higher residual is arisen by the difference between the real observed value and experimentalists' choices, so that R-square value becomes lower. In this way, although R-square values of methane and ethylene are low, the implication, that the correlation between carbon source concentration and temperature for methane and ethylene exists, still could be drawn from the linear regression, due to the presence of good P-values.

As shown in Fig. 7, temperature is positively correlated with methane and ethylene concentration, while independent with acetylene concentration. As discussed in 3.1, nonspecific catalyst employed in the experiments via three kinds of carbon source and diffusion process of direct carbon precursor through catalyst nanoparticles could not be the primary reasons to explain the distinction in the performance of temperature. It probably results from the process of carbon sources' thermal conversion to form direct carbon precursor and carbon nanotubes. The additional energy provided by higher temperature is consumed by the additional carbon source. It suggests the presence of thermal conversion of methane and ethylene. If the thermal conversion does not exist for methane and ethylene, successful syntheses should be observed at 800-850 ℃ and $9.00x10^{-6}$ – $1.10x10^{-5}$ mol/cm^3 for methane, as well as at 750℃ and $2.00x10^{-6}$ mol/cm^3 for ethylene, because successful experiments have been achieved at lower carbon source

concentration associated with the same temperature; Further, methane and ethylene could be the direct carbon precursor. The additional direct carbon precursor that far away from the catalyst surface would not demand for additional energy, due to the surface effect of the catalyst. The direct carbon precursor near the catalyst surface has been sufficient to utilize the catalysts, which have been oversaturated. Then the reaction between direct carbon precursor and catalyst could be restricted to the catalyst surface.

On the other hand, high acetylene concentration was not necessarily associated with high temperature to achieve successful synthesis (Fig. 8). The additional energy is not required by the additional acetylene. It probably suggests that acetylene could be the direct carbon precursor or easily get access to it. In the CNT growth process, catalyst nanoparticls have already been oversaturated, according to VLS mechanism. Now, only the direct CNT precursors near the catalyst nanoparticles contribute to the CNT growth, due to the surface effect of catalysts. Here, an adequate temperature (e.g., around 700℃ in my data set) has already been available to drive the growth at both low and high acetylene concentration (0-5x10^{-6} mol/cm^3). Thus, the additional acetylene does not contribute to the synthesis. If so, the temperature required in the experiments via acetylene (e.g., around 700℃ in my data set) could only be the requirement for the diffusion through catalyst and incorporation of carbon nanotubes.

These trends are counterintuitive. One would expect that, for a thermal conversion dominated process, if fraction of active molecules increases with temperature,

then less carbon source would be needed at high temperature. However, that is not seen here. It could be due to scatter in the data (e.g., the operators' choice being wide in this space) or the lack of limitation that growth rate should stay the same.

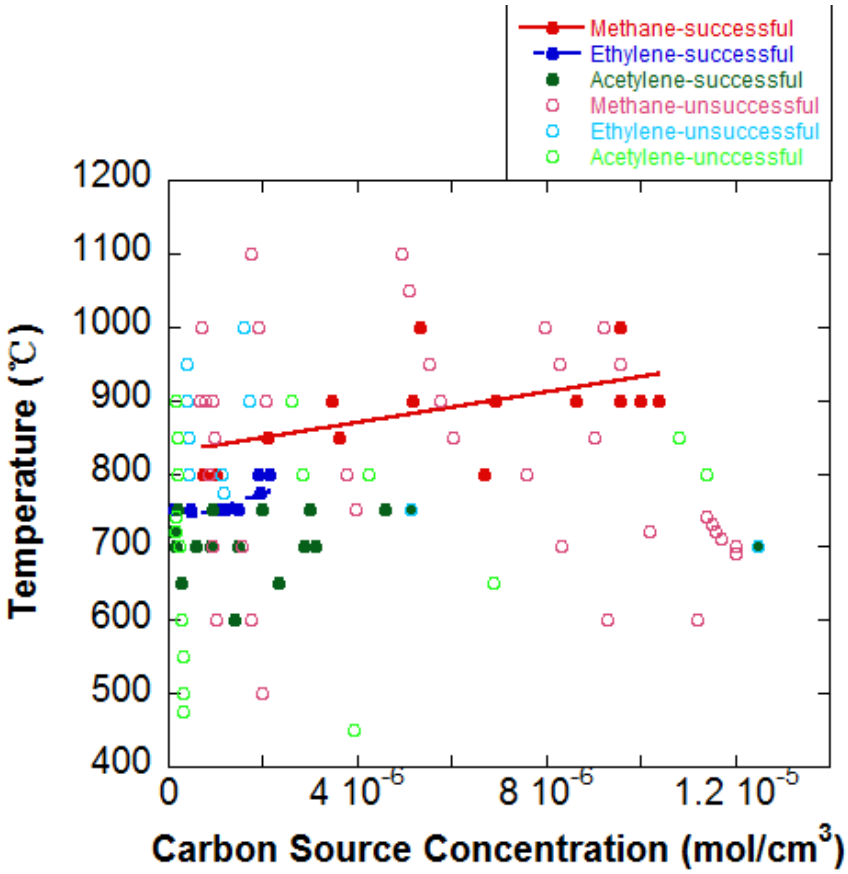


Figure 7: Correlated selection of carbon source concentration (mol/cm³) and temperature (℃) for successful experiments via methane, ethylene and ethylene (unsuccessful experiments included in the figure), showing the best fit linear regression models for successful experiments.

Table 3: Statistical analysis for the linear regression of carbon source concentration and temperature employed in the successful synthesis.

Carbon Source	Regression Coefficients ±Standard Error	Intercept ±Standard Error	P-value	R^2	Observations
Methane	$(1.0\pm0.4)\times10^7$	$(83\pm3)\times10$	0.01	0.31	21
Ethylene	$(2.1\pm0.6)\times10^7$	$(73\pm1)\times10$	0.01	0.44	17
Acetylene			0.95	0.01	21

3.2.3 Effects of Carbon Source Concentration associated with Temperature on Growth Rate

Fig. 8 shows the effect of carbon source concentration associated with temperature on the growth rate of carbon nanotubes achieved in the successful experiments. Here, growth rate is employed to further compare the quality of these successful experiments, so that further implications could be achieved.

As shown in figure 8 (b), high growth rates of carbon nanotubes in experiments via ethylene are observed in the area just around the regression line shown in Fig.7 , from 1.00×10^{-6} mol/cm^3 of ethylene at 700 ℃ to 1.90×10^{-6} mol/cm^3 of ethylene at 800 ℃. When the experiments conditions were restricted to this correlative relation, the energy input would be sufficient to best match kinetic requirements by ethylene to achieve sufficient formation of direct CNT precursors. At points beyond the regression line, the redundant energy input would suppress the activity of catalyst by increasing catalyst molecules' mobile rate so that the catalyst nanopariticles become too large, resulting in

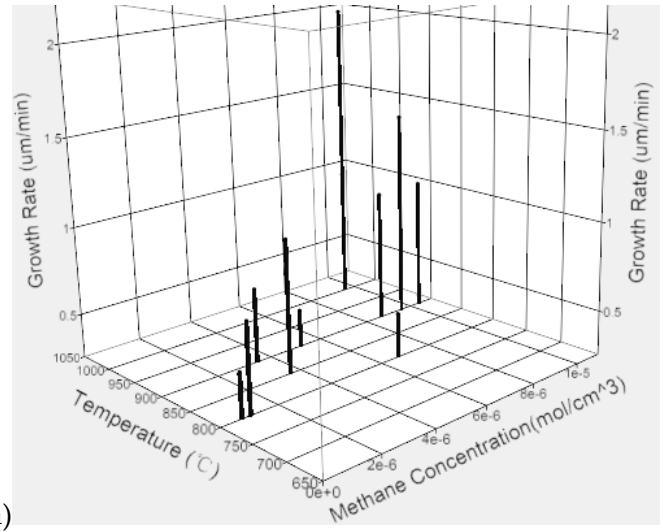
decline of growth rate or even unsuccessful synthesis [183]. While at points below the regression line, the low temperature would reduce the fraction of activated molecules, leading to less available molecules to go through reactions and less formation of direct CNT precursors. In this way, high growth rate via ethylene could be achieved when temperature and ethylene concentration are correlated following the relation shown by regression line.

In addition, high growth rates of carbon nanotubes for experiments via methane are observed in the area of high methane concentration of $9.00x10^{-6}$- $10.0x10^{-5}$ and high temperature of 900-1000℃ (Fig. 8(a)), rather than all of the area around the regression line. The lack of high growth rate at low methane concentration with relatively low temperature implies near the regression line that methane probably employs high activation energy to go through reactions. Low concentration of methane does not demands for energy as more as high concentration, and the relatively low temperature has been sufficient to provide energy for the formation of direct carbon precursor; however, the low temperature declines the fraction of activated molecule and total energy input, resulting in the situation that few activated molecule could accomplish the activation to form direct carbon precursors. Then high growth rate is not observed at low methane concentration with low temperature around regression line, due to the limited accomplishment of thermal conversion and less direct CNT precursors, although the experiments in this area were indeed successful. Also, high methane concentration at

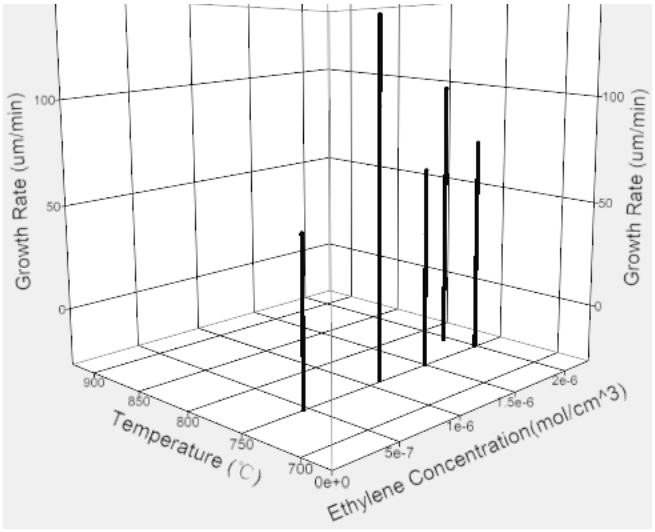
high temperature helps to achieve high growth rate by the sufficient formation of direct carbon precursor, benefiting from sufficient energy for more activated molecules.

In terms of acetylene, the figure clearly shows that acetylene concentration do not contribution to growth rate of carbon nanotubes, which just increases over temperature (Fig. 8(c)). It supports the previous discussion that acetylene could be the direct carbon precursor, because additional acetylene do not demand for additional energy, referring to acetylene does not require thermal conversion to form a specific intermediate product before CNT incorporation. The growth rate could be only restricted to the surface effect of catalyst in respects of material. High temperature promotes the reaction by accelerating kinetic rate of molecules to increase the probability that effective collision occurs, so that it contributes to the incorporation of carbon nanotubes.

Note, the regression lines of the successful growth experiments cannot be statistically differentiated from that of the unsuccessful experiments.


Growth Rate (um/min)
2
1.5
1
0.5
1050
1000
950
900
850
800
750
700
650
Temperature (℃)
0e+0
2e-6
4e-6
6e-6
8e-6
1e-5
Methane Concentration(mol/cm^3)
Growth Rate (um/min)

(a)


Growth Rate (um/min)
100
50
0
900
850
800
750
700
Temperature (℃)
0e+0
5e-7
1e-6
1.5e-6
2e-6
Ethylene Concentration(mol/cm^3)
Growth Rate (um/min)

(b)

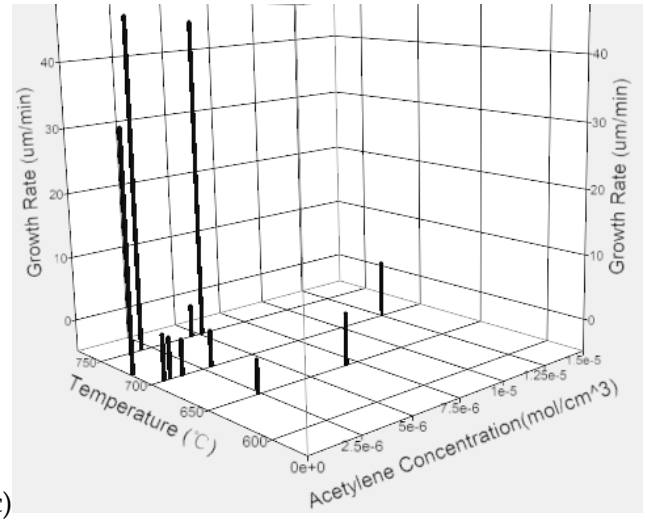
(c) 

Figure 8: Effects of carbon source concentration associated with temperature employed in the successful syntheses on: (a) Growth rate of CNTs via mathane (um/min); (b) Growth rate of CNTs via ethylene (um/min); (c) Growth rate of CNTs via acetylene (um/min).

3.3 Effects of Hydrogen Concentration associated with Temperature on Synthesis

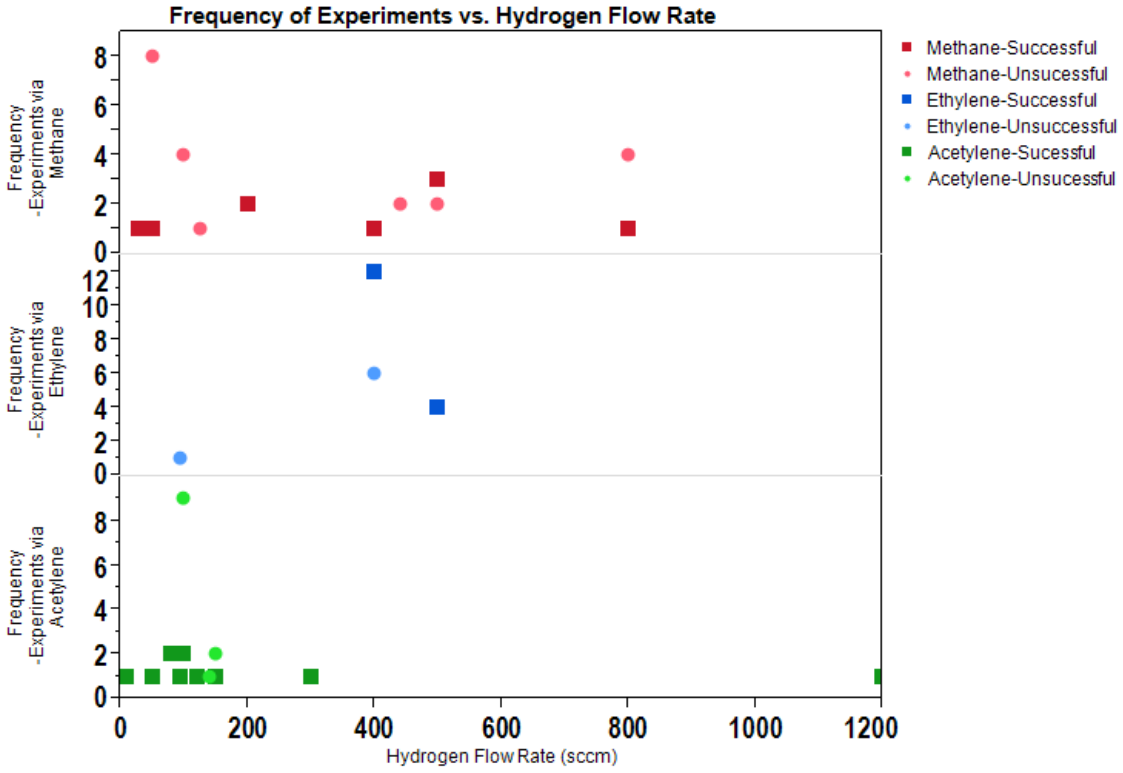
3.3.1 Effects of Carbon Source Flow Rate on Successful Rates of Synthesis

As shown in Fig. 9(a) and (b), the successful experiments via methane are observed in a wide range of hydrogen flow rate in 0-600 sccm, while successful experiments via ethylene and acetylene gather in a respectively smaller range of 400-600 sccm and 0-200 sccm. This figure just works as a summary for people's selection of hydrogen flow rate. According to table 4, success rates of experiment respectively via methane, ethylene and acetylene vary over hydrogen flow rate. The distinction in success rate at each value for every specific carbon source implies that hydrogen flow rate may have influence on the synthesis .Hydrogen flow rates of 500-600 sccm seem to be suitable for experiments via methane, because relatively high success rates and frequencies of successful experiments are stay in this range; similarly, hydrogen flow rates of 400-500 sccm and 100-200sccm are respectively suitable for experiments via ethylene and acetylene. It could easily lead us to come up with implications that methane and ethylene demand for more hydrogen than acetylene. However, similarly with carbon source concentration, hydrogen concentration should be calculated to eliminate the difference of reactor volume and essentially reveal the amount of carbon source. Also, the calculated hydrogen concentrations represent the total concentration of

hydrogen in the reactor before participating in the reactions. In other words, it represents the "start concentration" without reactions, and different with the hydrogen concentration at equilibrium.

As kind of material indicator, effects of hydrogen concentration was also investigated associated with temperature, which is kind of energy indicator, to check whether there is correlation to make energy thermodynamically favorable and kinetically possible for the materials in successful experiments so that implications on chemical mechanism and life-cycle assessment could be achieved

(a)



(b)

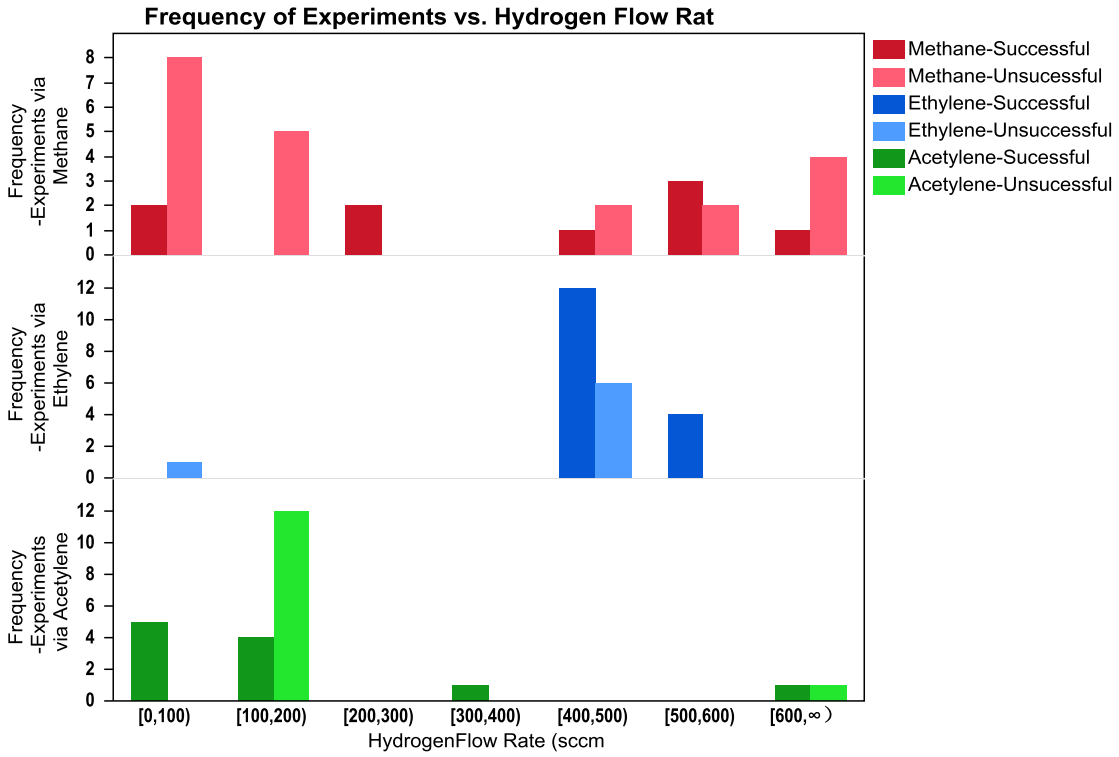


Figure 9: Frequency distribution of Hydrogen flow rate (sccm) for synthesis via three kinds of carbon source: (a) Initial samples of Hydrogen flow rate (sccm); (b) resample with 100sccm bins.

Table 4: Success rates of experiment in hydrogen flow rate groups with 100 sccm bins.

	[0，100)	[100,200)	[200,300)	[300,400)	[400,500)	[500,600)	[600,∞）
Methane	20%	0	100%		33%	60%	20%
Ethylene	0				67%	100%	
Acetylene	100%	25%		100%			50%

3.3.2 Correlation Analysis between Hydrogen Concentration and Temperature for Successful Syntheses

Fig. 10 summarizes the hydrogen concentrations and correspondent temperature for each successful and unsuccessful synthesis respectively via methane, ethylene and acetylene. The values of hydrogen concentration for experiments respectively via three types of carbon source do not quantitatively indicate a distinction in demand for hydrogen, in contrast to the discussion in 3.3.1 that methane and ethylene probably demand for more hydrogen than acetylene.

According to Table 5, regressions between hydrogen concentration and temperature for successful experiments via methane and ethylene have low p-values (< 0.05), referring to that linear interaction is positively significant between hydrogen concentration and temperature employed in the successful experiments; whereas, hydrogen concentration for acetylene is independent to the temperature to make the synthesis successful. The linear correlations of hydrogen concentration to temperature could also be false appearances arisen from the linear correlations between temperature concentrations of methane and ethylene, when hydrogen concentration is positively correlated to carbon source concentration. However, this possibility has been denied by the later discussion on effects of hydrogen/carbon source ratio. In addition, despite of inadequate R-square values, the presence of good P-values still enable us to draw implications from this figure.

As shown in Fig. 10, temperature is positively correlated with hydrogen concentration in the successful experiments via methane and ethylene, while independent with hydrogen concentration for acetylene. It has been reported that hydrogen works as reducing agent to provide electrons to catalyst and maintain catalysts' activity [11]. Due to surface effect of catalyst, the energy required by this reduction process might be constant. In this figure, additional energy demand is not observed at high hydrogen concentration for successful acetylene experiments. This indicates that synthesis via acetylene does not demand for hydrogen to carry out other reactions except the reduction of catalyst. Conversely, the additional energy demand is observed for successful methane and ethylene experiments. Thus, hydrogen would participate in the thermal conversion process, required by methane and ethylene, whereas it may not be required in the thermal conversion of acetylene.

Note, the regression lines of the successful growth experiments cannot be statistically differentiated from that of the unsuccessful experiments.

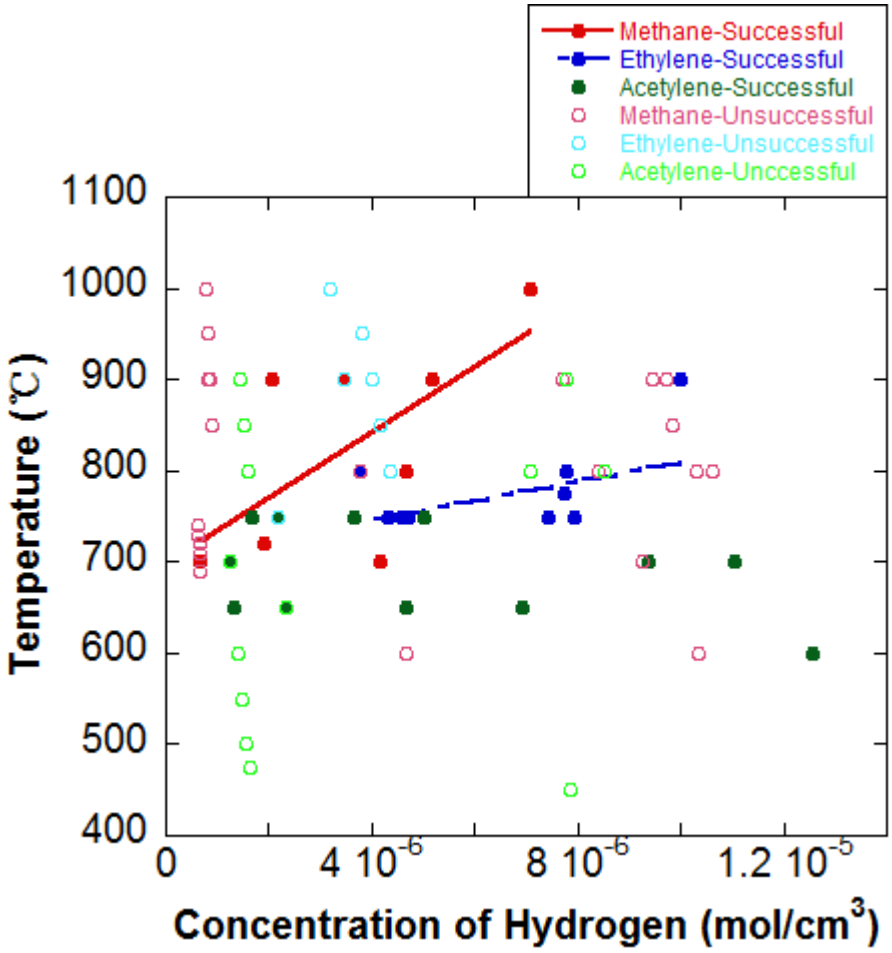


Figure 10: Correlated selection of hydrogen concentration (mol/cm³) and temperature (℃) for successful experiments via methane, ethylene and ethylene (unsuccessful experiments included in the figure), showing the best fit linear regression models for successful experiments.

Table 5: Statistical analysis for the linear regression of hydrogen concentration and temperature employed in the successful synthesis.

Carbon Source	Regression Coefficients ±Standard Error	Intercept ±Standard Error	P-value	R^2	Observations
Methane	(3.6±0.2)x10⁷	(70±7)x10	0.05	0.43	9
Ethylene	(1.0±0.5)x10⁷	(70±3)x10	0.05	0.26	16
Acetylene			0.21	0.15	12

3.3.3 Effects of Hydrogen Concentration associated with Temperature on Growth Rate

Fig. 11 shows the effect of hydrogen concentration associated with temperature on the growth rate of carbon nanotubes achieved in the successful experiments. As shown in Fig. 11 (a), hydrogen prompts the carbon nanotube growth by reducing the catalysts with more energy input provided by increasing temperature, so that the growth rate is increasing from condition with a hydrogen concentration of 2.00×10^{-6} mol/cm^3 at approximately 720 ℃ to condition with a hydrogen concentration of 3.20×10^{-6} mol/cm^3 at approximately 740 ℃, following the increasing regression line. However, the growth rate begins to decrease at even higher hydrogen concentration with higher temperature. As previous discussion, 900 ℃ was optimum for successful experiments via methane; further, temperature would not account for the drop of growth rate. In this way, high concentration of hydrogen would suppress the carbon nanotube growth, leading us to hypotheses that hydrogen participate in the thermal conversion process of methane or reaction with carbon nanotube products.

At first, hydrogen would affect growth rate by participating in the reverse reaction with solid carbon to form hydrocarbon (i.e., methane). Carbon could be deposited on catalysts in several forms (e.g., graphite, carbon nanotubes and amorphous carbon). Bronikowski et al. (2006) reported that the growth rate of carbon nanotubes

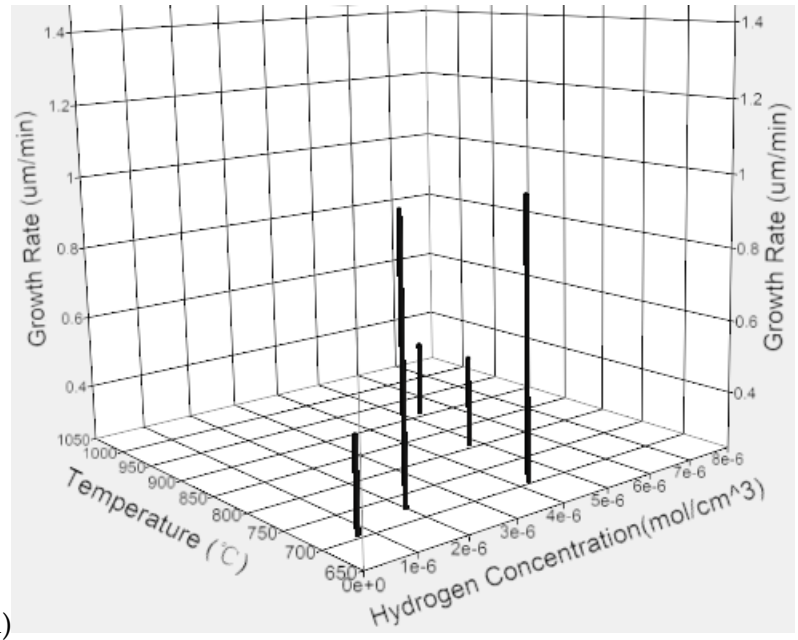
will depend on the rates of the competing reactions of the thermal conversion of methane and the reaction of hydrogen with solid carbon to form methane, which further depend on the concentrations of methane and hydrogen Moreover, these different forms of carbon employs varying energy (e.g., carbon in the form of graphite is more stable and lower in energy than carbon nanotubes, which is further more energetically stable than amorphous carbon). Thus, hydrogen may prefer to react more with amorphous carbon than with carbon nanotubes, because the former is less stable and in higher energy state. Thus, the form, in which carbon is deposited, will sensitively depend on the concentration of hydrogen. Here, hydrogen may firstly react with amorphous carbon and form methane, resulting in increasing growth rate at low hydrogen concentration; nevertheless, it begins to react with carbon nanotube products at even higher hydrogen concentration, resulting in the decreasing growth rate. However, the reverse reaction between hydrogen and solid carbon to form methane has been reported to be carried out at temperatures higher than 900 ℃ [183]. Then it cannot well explain what is observed in my work at temperature lower than 900 ℃ as shown in the figure 12(a).

The other theory, which works to explain this observation, is the "polymerization-like formation mechanism" [174]. As Desiree et al.'s (2012) hypothesis, both ethylene and methane need to convert to acetylene. Ethylene and acetylene have been proved to carry out reactions to form intermediates [174]. Metal catalysts require to be reduced to remain the catalytic activity by hydrogen, resulting from that electrons

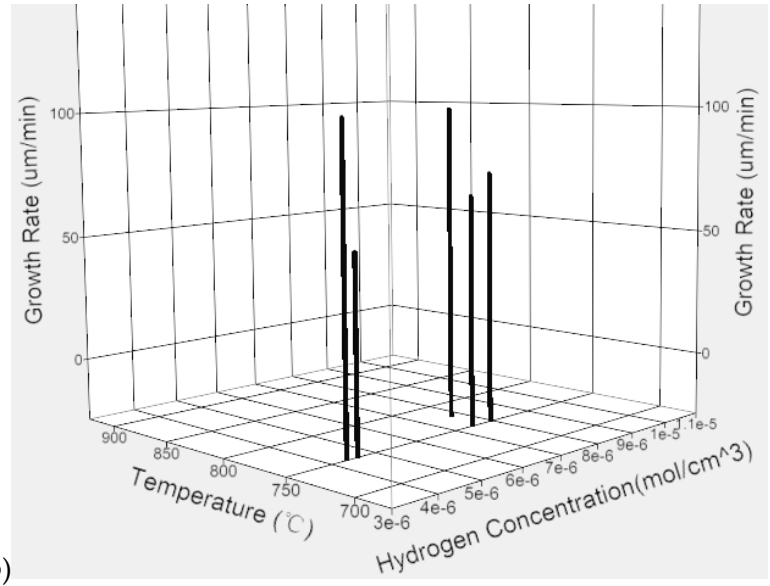
helps the bond formation. However, high concentration of hydrogen would terminate chain propagation by blocking monomer addition [174]. In this way, the inhibition of high hydrogen concentration on growth rate supports the "polymerization-like formation mechanism" as well as the thermal conversion of methane to ethylene and acetylene.

In figure 11 (b), the inhibition of high hydrogen concentration on growth rate is not observed; however, it does not reject to "polymerization-like formation mechanism", due to the missing value at high temperature. On the other hand, the growth rates achieved in the experiments via ethylene are extraordinarily higher than methane and even acetylene. Since acetylene could be the direct carbon precursor, there is no reason to explain the extremely high growth rate of experiments via ethylene, according to VLS mechanism; however, it could be explained by the polymerization-like formation mechanism, because the acetylene would present in ethylene environment by the thermal conversion of ethylene.

As shown in figure 11 (c), a gradient of growth rate is not observed over hydrogen concentration in experiments via acetylene. It supports that additional hydrogen does not contribute to the experiments via acetylene.


Growth Rate (um/min)
1.4
1.2
1
0.8
0.6
0.4
1050
1000
950
900
850
800
750
700
650
Temperature (℃)
0e+0
1e-6
2e-6
3e-6
4e-6
5e-6
6e-6
7e-6
8e-6
Hydrogen Concentration(mol/cm^3)
Growth Rate (um/min)

(a)


Growth Rate (um/min)
100
50
0
900
850
800
750
700
Temperature (℃)
3e-6
4e-6
5e-6
6e-6
7e-6
8e-6
9e-6
1e-5
1e-5
Hydrogen Concentration(mol/cm^3)
Growth Rate (um/min)

(b)

(c)

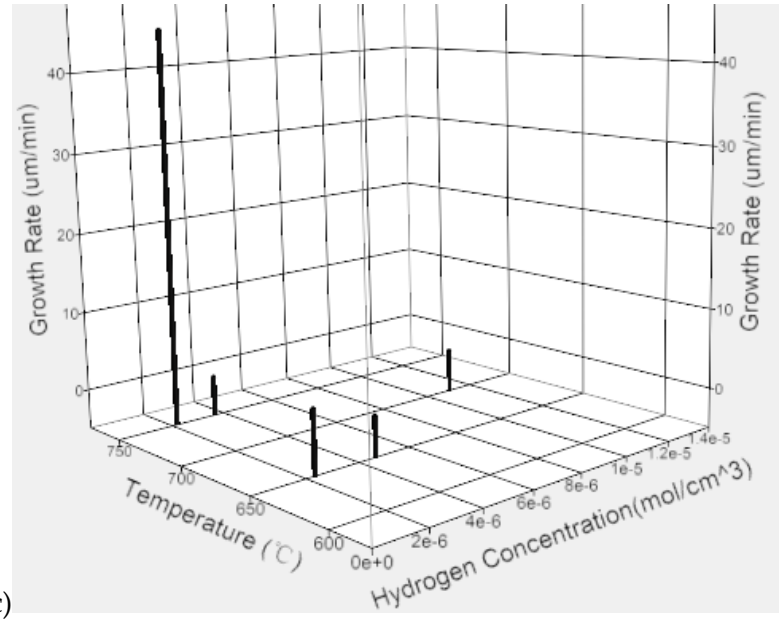
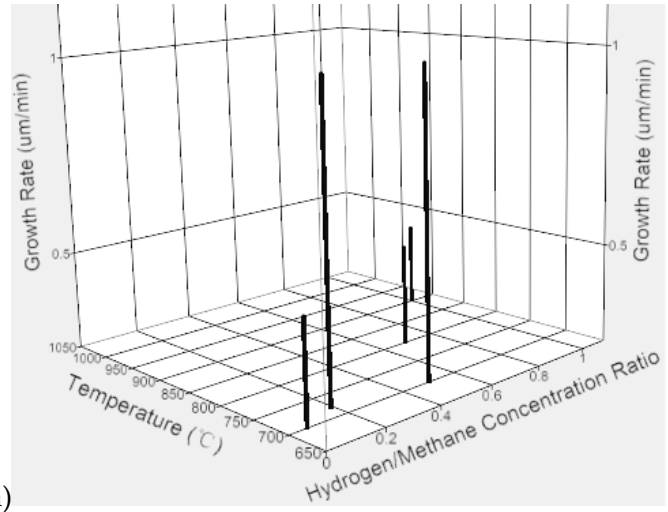


Figure 11: Effects of hydrogen concentration associated with temperature employed in the successful syntheses on: (a) Growth rate of CNTs via mathane (um/min); (b) Growth rate of CNTs via ethylene (um/min); (c) Growth rate of CNTs via acetylene (um/min).

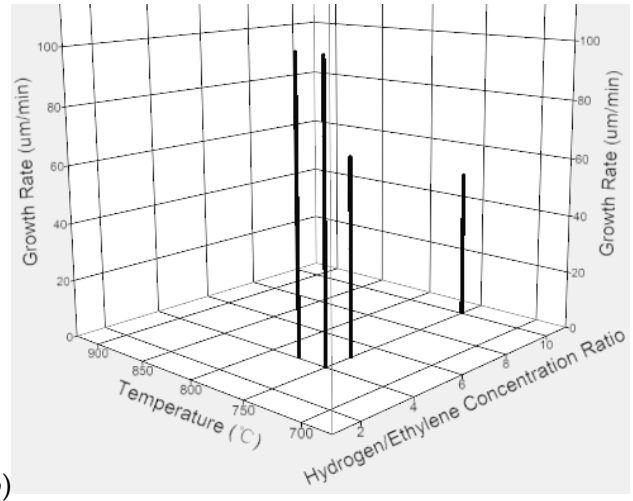
3.3.4 Effects of Hydrogen/Carbon Source Concentration Ratio associated with Temperature on Growth Rate

Figure 12 (a) and (c) are in accordance with figure 11 (a) and (c). It repeatly supports the promotion of low hydrogen concentration to growth of carbon nanotubes by reducing the catalysts, and the inhibition of high hydrogen concentration by terminating the chain propagation to form intermediates, as well as the thermal conversion of methane to ethylene and acetylene, just as discussed in 3.3.3. In addition, additional hydrogen does not contribute to the experiments via acetylene.

However, growth rate of carbon nanotubes in experiments via ethylene decreases over hydrogen/ethylene concentration ratio (Fig. 12 (b)). It nicely suggests that growth rate of carbon nanotubes in experiments via ethylene also decline at relatively high hydrogen concentration. Thus, Fig 11 (b) and 12 (b) jointly supports the existence of entire "polymerization-like formation mechanism" for experiments via ethylene.



(a)



(b)

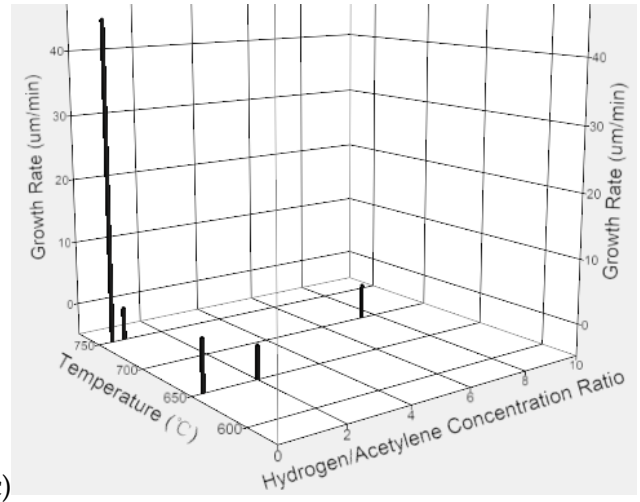
(c) 

Figure 12: Effects of hydrogen/carbon source concentration ratio associated with temperature employed in the successful syntheses on: (a) Growth rate of CNTs via mathane (um/min); (b) Growth rate of CNTs via ethylene (um/min); (c) Growth rate of CNTs via acetylene (um/min).

3.4 Effects of Residence Time associated with Temperature on Synthesis

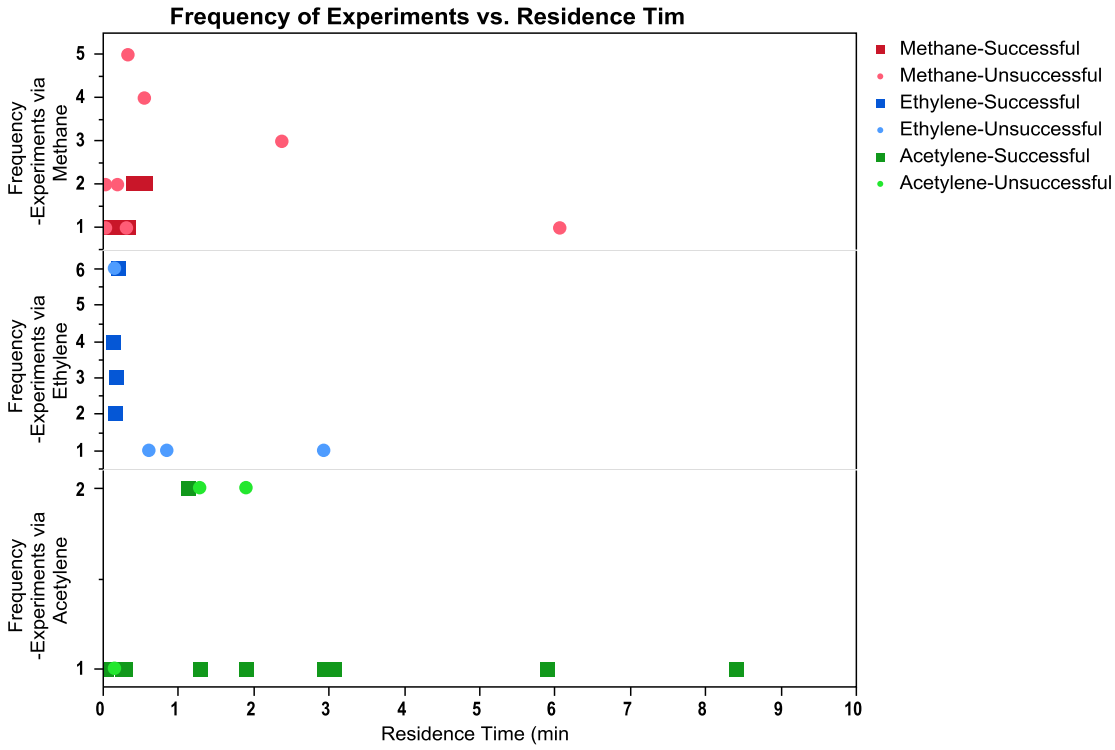
3.4.1 Effects of Residence Time on Successful Rates of Synthesis

Fig. 13(a) summarized the frequency of successful and unsuccessful experiments respectively via methane, ethylene and acetylene at each value of residence time. According to table 6, success rates of experiment respectively via methane, ethylene and acetylene vary over residence time. The distinction in success rate at each value of residence time implies that residence time may have influence on the synthesis.

The successful experiments via methane and ethylene are respectively observed in a range of 0-0.6 min and 0-0.2 min, which were all lower than 1 min; whereas, the experiments via acetylene can employ a residence time higher than 1 min to successfully synthesize carbon nanotubes.

Effects of residence time was also investigated associated with temperature to check whether there is correlation to make energy thermodynamically favorable and kinetically possible for the materials in successful experiments so that implications on chemical mechanism and life-cycle assessment could be achieved.

(a)


Frequency of Experiments vs. Residence Tim
Frequency -Experiments via Methane
Frequency -Experiments via Ethylene
Frequency -Experiments via Acetylene
Residence Time (min
Methane-Successful
Methane-Unsuccessful
Ethylene-Successful
Ethylene-Unsuccessful
Acetylene-Successful
Acetylene-Unsuccessful

(b)

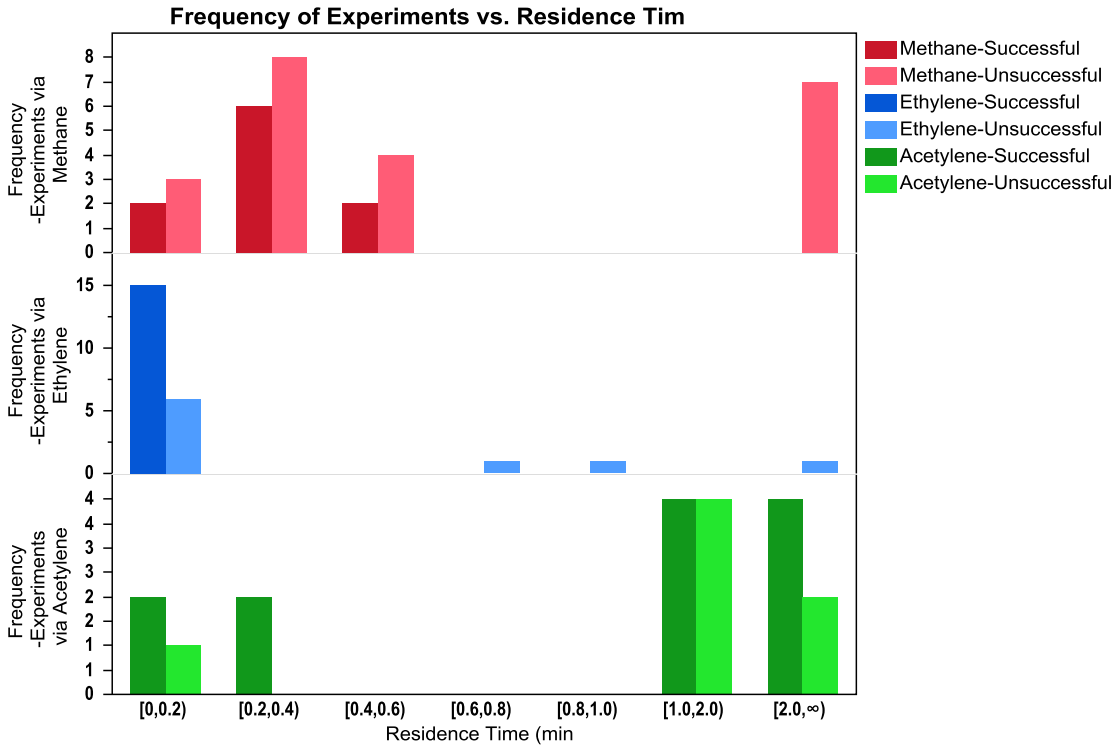


Figure 13: Frequency distribution of Residence Time (min) for synthesis via three kinds of carbon source: (a) Initial samples of Hydrogen flow rate (min); (b) resample with 0.2 min bins..

Table 6: Success rates of experiment in residence time with 0.2 min bins.

	[0,0.2)	[0.2,0.4)	[0.4,0.6)	[0.6,0.8)	[0.8,1.0)	[1.0,2.0)	[2.0,∞）
Methane	40%	43%	33%				0
Ethylene	75%			0	0		0
Acetylene	67%	100%				50%	67%

3.4.2 Correlation Analysis between Residence Time and Temperature for Successful Syntheses

Fig. 14 summarizes the residence time and correspondent temperature for each successful and unsuccessful synthesis respectively via methane, ethylene and acetylene. According to Table 7, regressions between residence time and temperature for successful experiments via methane and ethylene have low p-values (< 0.05), referring to that linear interaction is positively significant between residence time and temperature employed in the successful experiments; whereas, residence time for acetylene is independent to the temperature to make the synthesis successful.

Residence time refers to the average amount of time that a particle stays in the reactor. Meanwhile, residence time could be negatively correlated to flow velocity. At low residence time, molecules of methane and ethylene will not accumulate in the reactor, resulting in a low carbon source concentration and less energy demand; whereas, these molecules could accumulate in the reactor with a high carbon source concentration at relatively high residence time. However, short residence times could imply a large amount of waste if the rate of flow past the catalyst is faster than the rate of the reaction.

The high carbon source concentration at high temperature would lead to sufficient formation of direct carbon precursor. Then, a high growth rate of carbon nanotubes could be expected. However, at extremely high residence time, methane and ethylene have been reacted without sufficient carbon source supply. Then a large

number of byproducts would accumulate in the reactor, resulting in the decline in growth rate of carbon nanotubes. In this way, an optimum residence time could exist.

These trends are counterintuitive. One would expect that, for a thermal conversion dominated process, shorter residence times would require higher temperatures in order to achieve the appropriate thermal conversion in the shorter amount of time. However, that is not seen here. It could be due to scatter in the data (e.g., the operators' choice being wide in this space) or suggest that the thermal conversions are fast relative to transport time and relative reaction time at the catalyst.

Note, the regression lines of the successful growth experiments cannot be statistically differentiated from that of the unsuccessful experiments.

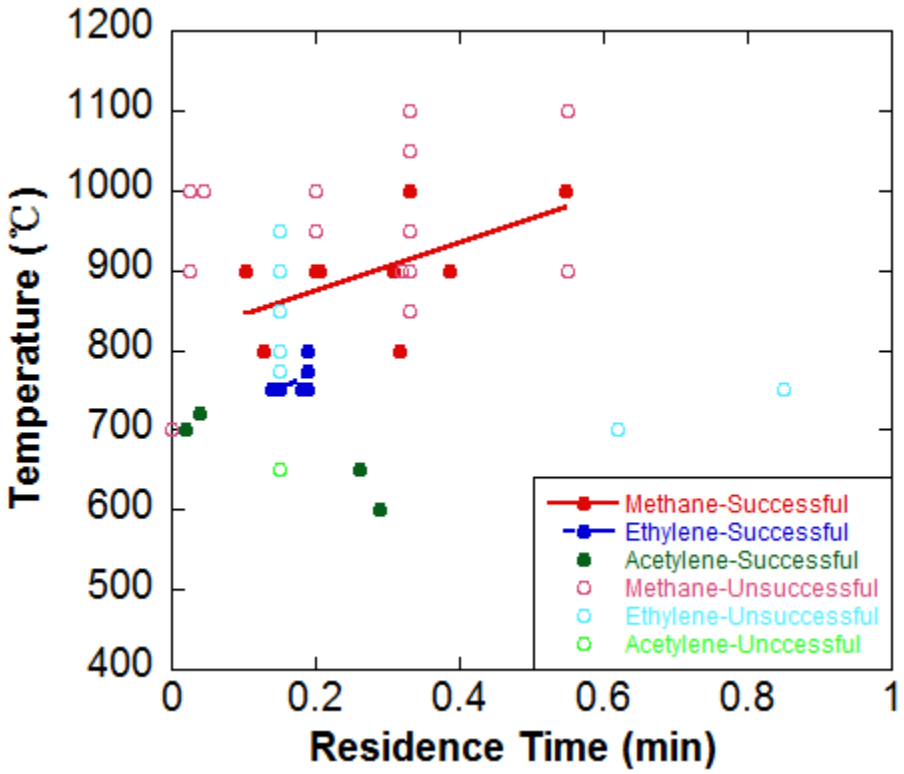


Figure 14: Correlated selection of residence time (min) and temperature (℃) for successful experiments via methane, ethylene and ethylene (unsuccessful experiments included in the figure), showing the best fit linear regression models for successful experiments.

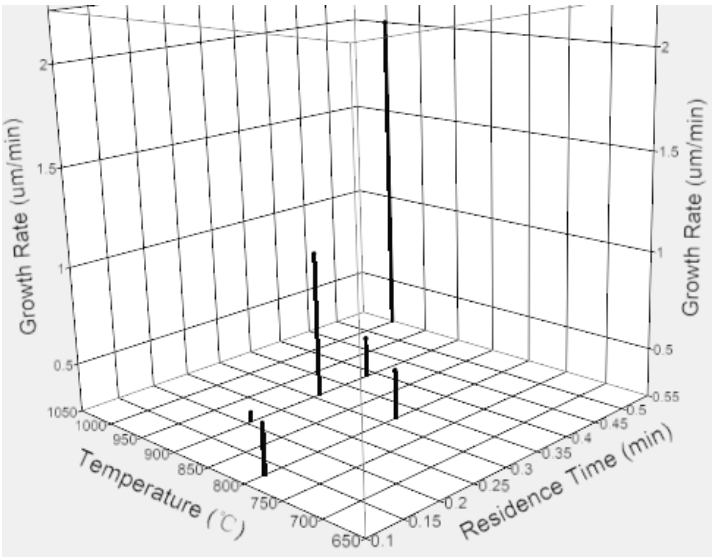
Table 7: Statistical analysis for the linear regression of residence time and temperature employed in the successful synthesis.

Carbon Source	Regression Coefficients ±Standard Error	Intercept ±Standard Error	P-value	R^2	Observations
Methane	(3±1)x10^2	(82±4)x10	0.04	0.41	11
Ethylene	(4±1) x10^2	(69±3)x10	0.01	0.39	15
Acetylene			0.76	0.10	8

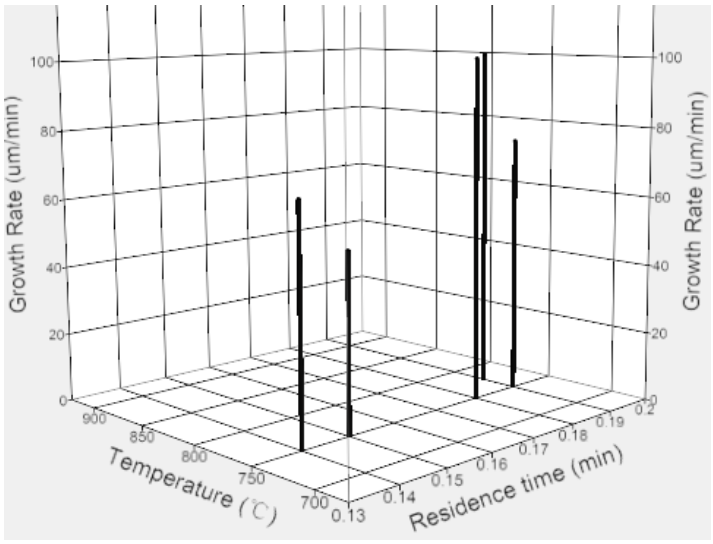
3.4.3 Effects of Residence Time associated with Temperature on Growth Rate

As shown in Fig. 15 (a), the highest growth rate in experiments via methane is observed in the area with residence time of 0.50-0.55 min and temperature of 1000 ℃. The growth rate decreases at lower residence time, because of the less carbon source accumulation. In addition, although the distribution of growth rate at residence time higher than 0.5 min cannot be discussed due to the limited data set, 0.50-0.55 still takes the possibility to be the optimum residence time for carbon. The residence lower than 0.5 min would cause a waste of carbon source; but it could help to maintain a lower energy demand.

As discussed in 3.2.3, ethylene probably employs a thermal conversion process with less activation energy demand than methane achieve a high growth rate at relatively low ethylene concentration with low temperature. Here, 0.18 min could be the optimum residence time for ethylene, associating with low temperature of 700 ℃. At too low residence time, carbon source could not be accumulated, causing a waste of material, while byproducts could be accumulated at too high residence time.


Growth Rate (um/min)
2
1.5
1
0.5
1050
1000
950
900
850
800
750
700
650
Temperature (℃)
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5
0.55
Residence Time (min)
Growth Rate (um/min)

(a)


Growth Rate (um/min)
100
80
60
40
20
0
900
850
800
750
700
Temperature (℃)
0.13
0.14
0.15
0.16
0.17
0.18
0.19
0.2
Residence time (min)
Growth Rate (um/min)

(b)

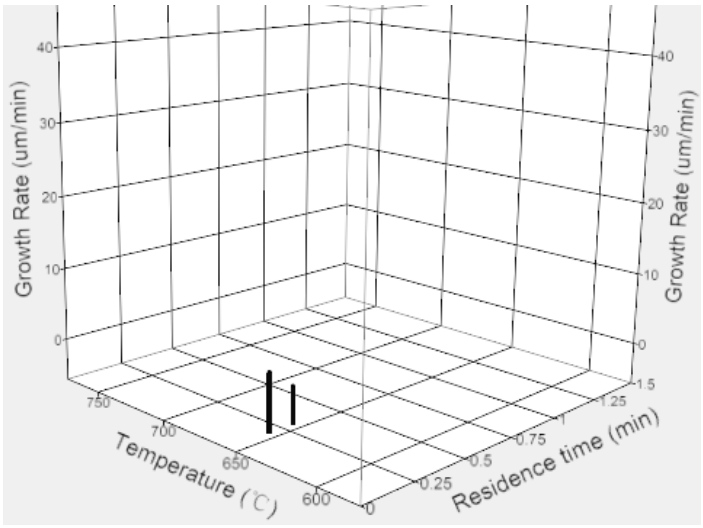
(c) 

Figure 15: Effects of residence time associated with temperature employed in the successful syntheses on: (a) Growth rate of CNTs via mathane (um/min); (b) Growth rate of CNTs via ethylene (um/min); (c) Growth rate of CNTs via acetylene (um/min).

4. Conclusions

In summary, methane employs more energy demand than ethylene, which in turn demands more energy than acetylene to successfully synthesize carbon nanotubes. The distinction in energy demand could be the result of kinetic energy requirements by the thermal conversion process of methane and ethylene to form direct CNT precursors, and methane employs the highest activation demand among three hydrocarbons. Thus, methane and ethylene could be thermally converted to form acetylene before CNT incorporation. This work also suggests that the energy required by thermal conversion processes of carbon source could dominate the synthesis temperature.

There could be an optimum residence time to maintain a relatively higher growth rate. At too low residence time, carbon source could not be accumulated, causing a waste of material; while too high residence time may cause the limitation of carbon source supplement and accumulation of byproducts.

At last, high concentration of carbon source and hydrogen could cause more energy consumption, while it helps to achieve a high growth rate, due to the more presence of direct carbon precursor.

In data collection, the lack of report in experimental conditions caused the limited data set in this work. Then valid observations on the statistically significant patterns between energy and materials were hindered by the limited data set. If a larger

repository for successful CNT syntheses did exist, then statistically significant patterns in the data might emerge to help us get access to more promising implications. Since complicated reaction process exists in CVD, which is also sensitivity to the experimental environment, the implications drawn from statistical analysis are required to be further investigated and checked by experiments.

Appendix A

Table 8: Data collection from papers on reactors [68-163, 184-188]

Order	Catalyst	Reactor Geometry	Reactor Dimensions (heated portion)	Types
1	Fe/Al_2O_3	cylindrical tube	22.9cm length x 4.8 mm diameter	Cold walled reactor
2	$FeCl_3$,Al/Fe, Al_2O_3/Fe, Al_2O_3/Co	cylindrical tube	38.1cm length x 25 mm diameter	Hot walled reactor
3	Fe/Al_2O_3	cylindrical tube		Hot walled reactor
4	Fe/Al_2O_3	cylindrical tube	1" diameter	Hot walled reactor
5	$FeCl_3$,Al/Fe, Al_2O_3/Fe, Al_2O_3/Co	cylindrical tube		Hot walled reactor
6	$FeCl_3$,Al/Fe, Al_2O_3/Fe, Al_2O_3/Co	cylindrical tube	38.1cm length x 25 mm diameter	Hot walled reactor
7	Fe/Al_2O_3	cylindrical tube	38.1cm length x 25 mm diameter	Hot walled reactor
8	Fe/Al_2O_3	cylindrical tube	30cm length x 22 mm diameter	Hot walled reactor
9	Fe/Al_2O_3	cylindrical tube	30cm length x 48 mm diameter	Cold walled reactor
10	Co/Mo	cylindrical tube	30cm length x 48 mm diameter	Cold walled reactor
11	Fe	cylindrical tube	30cm length x 48 mm diameter	Cold walled reactor
12	Fe/Al_2O_3	cylindrical tube	30cm length x 22 mm diameter	Hot walled reactor
13	Fe	cylindrical tube	30cm length x 22 mm diameter	Hot walled reactor
14	Fe/Al_2O_3	cylindrical tube	30cm length x 22 mm diameter	Hot walled reactor
15	Fe/Al_2O_3	cylindrical tube	30cm length x 48 mm diameter	Cold walled reactor
16	Fe/Al_2O_3	cylindrical tube	30cm length x 22 mm diameter	Hot walled reactor
17	Fe/Al_2O_3	cylindrical tube	7cm length x4 mm diameter	Cold walled reactor
18	Fe/Al_2O_3	cylindrical tube	1" diameter	Hot walled reactor

19	Fe/Al_2O_3	cylindrical tube	30cm length x 22 mm diameter	Hot walled reactor
20	Fe/Al_2O_3	cylindrical tube	30cm length x 22 mm diameter	Hot walled reactor
21	Fe/Al_2O_3	cylindrical tube	30cm length x 22 mm diameter	Hot walled reactor
22	Fe/Al_2O_3	cylindrical tube	30cm length x 22 mm diameter	Hot walled reactor
23	Fe/Al_2O_3	cylindrical tube	30cm length x 22 mm diameter	Hot walled reactor
24	$Fe_2Co/CaCO_3$	cylindrical tube	80 mm diameter	Hot walled reactor
25	$Co(Fe)/NaY/CaCO_3$	cylindrical tube	80 mm diameter	Hot walled reactor
26	$Fe_2Co/CaCO_3$	cylindrical tube	80 mm diameter	Hot walled reactor
27	$Fe_2Co/MgO/CaCO_3$	cylindrical tube	80 mm diameter	Hot walled reactor
28	$Fe_2Co/CaCO_3$	cylindrical tube	80 mm diameter	Hot walled reactor
29	$Fe_2Co/CaCO_3$	cylindrical tube	80 mm diameter	Hot walled reactor
30	Fe_2Co	cylindrical tube	80 mm diameter	Hot walled reactor
31	Fe_2Co	cylindrical tube	80 mm diameter	Hot walled reactor
32	$Fe/Co/Ni/CaCO_3$	cylindrical tube	80 mm diameter	Hot walled reactor
33	Fe_2Co	cylindrical tube	80 mm diameter	Hot walled reactor
34	Fe/Ni	cylindrical tube	80 mm diameter	Hot walled reactor
35	$Fe_2Co/CaCO_3$	cylindrical tube	80 mm diameter	Hot walled reactor
36	Fe_2O_3	cylindrical tube	1" diameter	Hot walled reactor
37	$Fe/Al_2O_3/Mo$	cylindrical tube	1" diameter	Hot walled reactor
38	Fe	cylindrical tube	2" diameter	Hot walled reactor
39	$Fe/Al_2O_3/Mo$	cylindrical tube	2" diameter	Hot walled reactor
40	$Fe/Al_2O_3/Mo$	cylindrical tube	1" diameter	Hot walled reactor
41	$Fe/Al_2O_3/Mo$	cylindrical tube	1" diameter	Hot walled reactor
42	$Al_2O_3/Fe(NO_3)_3/Mo_2(acac)_2$	cylindrical tube	1" diameter	Hot walled reactor
43	Fe_2O_3	cylindrical tube	1" diameter	Hot walled reactor

44	$Fe/Al_2O_3/Mo$	cylindrical tube	48" length x 4" diameter	Hot walled reactor(rotary)
45	Al_2O_3/Fe	cylindrical tube		Hot walled reactor
46	Fe_2O_3	cylindrical tube	1" diameter	Hot walled reactor
47	Al_2O_3/Fe	cylindrical tube		Hot walled reactor
48	$Fe/Al_2O_3/Mo$	cylindrical tube	1" diameter	Hot walled reactor
49	Fe_2O_3	cylindrical tube	1" diameter	Hot walled reactor
50	Fe	cylindrical tube	48" length x 5" diameter	Hot walled reactor(rotary)
51	Fe	cylindrical tube	48" length x 4" diameter	Hot walled reactor(rotary)
52	Fe-doped CAs	cylindrical tube	2.5cm length x 1cm diameter	Hot walled reactor
53	Fe	cylindrical tube	2ft length x 1" diameter	Hot walled reactor
54	Au	cylindrical tube	2.5 cm diameter	Hot walled reactor
55	$Fe(CO)_5$	cylindrical tube		Hot walled reactor
56	Fe/Mo	cylindrical tube		Hot walled reactor
57	CoO_x/AC	cylindrical tube	105cm length x 6cm diameter	Hot walled reactor
58	Fe/Mo	cylindrical tube		Hot walled reactor
59	$Fe/Co/CaCO_3$	cylindrical tube	20cm length x 1.2cm diameter	Hot walled reactor
60	Cu	cylindrical tube	3cm D	Hot walled reactor
61	$FeCl_3$	cylindrical tube	90cm length x 2.5 cm diameter	Hot walled reactor
62		cylindrical tube	0.038cm diameter	Filament
63	LaFeMoMnO	cylindrical tube	4cm diameter	Hot walled reactor
64	Fe/Al/Co	cylindrical tube	1cm diameter	Microwave Plasma
65	Fe	cylindrical tube		Hot walled reactor
66	Fe/Co	cylindrical tube		Hot walled reactor
67	Mo/Co	cylindrical tube	5.1cm diameter	Hot walled reactor

68	Mo/Co	cylindrical tube		Hot walled reactor
69	Fe/Co	cylindrical tube	2.54cm diameter	Hot walled reactor
70	Fe	cylindrical tube		Hot walled reactor
71	Fe/Al_2O_3	cylindrical tube	80 mm diameter	Hot walled reactor
72	stainless steel $_3 0_4$	cylindrical tube		Hot walled reactor
73	Fe_2O_3/MgO	cylindrical tube	70cm length x 3.2cm diameter	Hot walled reactor
74	Fe/Al_2O_3	cylindrical tube	130cm length x 6cm diameter	Hot walled reactor
75	$LaFexMoyMnzO_3$	cylindrical tube	4cm diameter	Hot walled reactor
76	Al_2O_3	cylindrical tube		Hot walled reactor
77	Ni/Y/Cu	cylindrical tube		Hot walled reactor
78	Fe	cylindrical tube	65cm length x 4cm diameter	Hot walled reactor
79	Mg/Mo	cylindrical tube		Hot walled reactor
80	palygorskite	cylindrical tube		Hot walled reactor
81	Fe/Ni	cylindrical tube		Hot walled reactor
82	Fe	cylindrical tube	8cm length x 5cm diameter	Hot walled reactor
83	Fe-Co/MgO	cylindrical tube		Hot walled reactor
84	Fe/Al_2O_3	cylindrical tube	2.54cm diameter	Hot walled reactor
85	$Fe/Mo/Al_2O_3$	cylindrical tube	120cm length x 7.5cm diameter	Hot walled reactor
86	$(Fe,Si)_3O_4$	cylindrical tube		Hot walled reactor
87	nano-$CaCO_3$	cylindrical tube		Hot walled reactor
88	Fe	cylindrical tube		Hot walled reactor
89	Ni	cylindrical tube		Hot walled reactor
90	Fe/Al_2O_3	cylindrical tube	20cm length x 2.5cm diameter	Hot walled reactor
91	Fe/Al_2O_3	cylindrical tube	5cm diameter	Hot walled reactor
92	Fe/Al_2O_3	cylindrical tube	16cm diameter	Hot walled reactor

93	Fe_2O_3/Al	cylindrical tube		Hot walled reactor
94	Fe/Co	cylindrical tube	20cm length x 1.8cm diameter	Hot walled reactor
95	Fe/MgO	cylindrical tube	25cm length x 4cm diameter	Hot walled reactor
96	Fe_{20}Mt	cylindrical tube		Hot walled reactor
97	Fe/Al_2O_3	cylindrical tube		Hot walled reactor
98	Fe/Co/Ni	cylindrical tube	100cm length x 4cm diameter	Hot walled reactor
99	Co	cylindrical tube		Hot walled reactor
100	Zr	cylindrical tube	50cm length x 3cm diameter	Hot walled reactor
101	Fe/Co/MgO	cylindrical tube	3cm diameter	Hot walled reactor
102	Fe	cylindrical tube		Hot walled reactor
103	Fe	cylindrical tube		Hot walled reactor
104	Fe	cylindrical tube		Hot walled reactor
105	Fe	cylindrical tube		Hot walled reactor
106	Fe	cylindrical tube		Hot walled reactor
107	Fe	cylindrical tube		Hot walled reactor
108	Fe	cylindrical tube		Hot walled reactor

Table 9: Data collection from papers on gas injections [68-163, 184-188]

Order	Carbon Source	Other Gases	Temperature of System (°C)	Flow Rate of Carbon(sccm)	Flow rate-Other gases(sccm)	Terminal Length of CNT (um)	Synthesis Time (min)
1	Ethylene	H_2,He	750	C_2H_4:70	H_2:330,He:70		
2	Ethylene	H_2,Ar or He,H_2O	750	C_2H_4:100	H_2:400,He:600	2500	10
3	Ethylene	H_2, He					
4	Ethylene	H_2, He	750	C_2H_4:100	H_2+He:1000	1400	10
5	Ethylene	H_2,Ar or He,H_2O	550-750				
6	Ethylene	H_2,Ar or He,H_2O	750	C_2H_4:100	H_2:400,He:600	2500	20
7	Ethylene	H_2,He	750	C_2H_4:100	H_2:400,He:600	1000	
8	Ethylene	H_2,Ar	750	C_2H_4:100	H_2:500,Ar:200	1000	15
9	Ethylene	H_2,Ar	810	C_2H_4:115	H_2:400,Ar:100	1500	15
10	Ethylene	H_2,CO	800	C_2H_4:115	H_2:400,CO:100	2000	15
11	Ethylene	H_2,CO	1000	C_2H_4:115	H_2:400,CO:100	2000	15
12	Ethylene	H_2,Ar	800-1200(800)	C_2H_4:100	H_2:500,Ar:200	1000	15
13	Ethylene	H_2,He	750				
14	Ethylene	H_2,He	750	C_2H_4:100	H_2:400,He:100	1500	20
15	Ethylene	H_2,He		C_2H_4:120	H_2:310,He:180	2900	25
16	Ethylene	H_2	750				
17	Ethylene	H_2,He	675-875(825)	C_2H_4:120	H_2:310,He:180	3500	15
18	Ethylene	H_2, He	750-800(750)	C_2H_4:120	H_2+He:1000	1500	
19	Ethylene	H_2,He	775	C_2H_4:100	H_2:400,He:100	2000	20
20	Ethylene	H_2,He	750-800(800)	C_2H_4:110	H_2:400,Ar:75		
21	Ethylene	H_2,He	775	C_2H_4:100	H_2:400,He:100	2000	20

22	Ethylene	H_2,He	775	C_2H_4:100	H_2:400,He:100	2000	20
23	Ethylene	H_2,He	775	C_2H_4:100	H_2:400,He:100	2000	20
24	Acetylene	N_2	700-740(700)	C_2H_2:16.67	N_2:1166.67		
25	Acetylene	H_2,N_2	700-800(750)		H_2:8,N_2:75		
26	Acetylene	N_2	680-740(680)	C_2H_2:50	Ar:150		
27	Acetylene	CO_2	660-820(660)				
28	Acetylene	CO_2,Ar	640	C_2H_2:16.67,CO_2:16.67	Ar:750		
29	Acetylene	H_2,Ar	750	C_2H_2:50-400(225)	Ar:100-300(200),H_2:40-150(95)	950	30
30	Acetylene	CO_2,Ar	400-600(500)	C_2H_2:16.67,CO_2:16.67	Ar:750		
31	Acetylene	CO_2,Ar	640	C_2H_2:16.67,CO_2:16.67	Ar:750		
32	Acetylene	CO_2,Ar	350-850(675)	C_2H_2:166.67	Ar:1333.33		
33	Acetylene	H_2,Ar	750	C_2H_2:50-200(100)	H_2:80,Ar:80	1350	30
34	Ethylene	H_2,Ar	650-750(660)	C_2H_4:16.67	H_2:16.67,Ar:116.67		
35	Acetylene	CO_2,Ar	500-600(600)	C_2H_2:16.67,CO_2:16.67	Ar:750		
36	Methane	H_2,Ar	1000	CH_4:6150		10	10
37	Methane	H_2,Ar	1000	CH_4:1000-6000(3500)		20	10
38	Ethylene		700	C_2H_4:1000		10	15
39	Methane	H_2,Ar	850-1000(900)			10	15
40	Methane	H_2,Ar	900	CH_4:6000		30	30
41	Methane	H_2,Ar	900	CH_4:750		6	20
42	Methane	H_2,Ar	900	CH_4:5000			
43	Methane	H_2,Ar	900	CH_4:200	H_2:200		
44	Methane	H_2	900	CH_4:1500	H_2:50-150(125)	10	7

45	Methane		850-1000				
46	Methane	H_2,Ar	900	CH_4:200	H_2:200	0.5-5	5
47	Ethylene		700				
48	Methane	H_2,Ar	800	CH_4:720,C_2H_4:24	H_2:500	3	2
49	Methane	H_2	900	CH_4:1000,C_2H_4:20	H_2:500	100	10
50	Methane	Ar	600	CH_4:48	Ar:12	0.3	3
51	Methane	H_2,O_2	720	CH_4:160	H_2:30,O_2:2.4	10	10
52	Methane	H_2,Ar	600-800(700)	CH_4:1000,C_2H_4:20	H_2:500	10	10
53	Methanol	H_2,Ar	925		H_2:440,Ar:600		20
54	Methane	H_2,Ar	800-900(800)	CH_4:30,C_2H_4:20	H_2:440	15	10
55	Ethylene	H_2,Ar	800-1000(900)	C_2H_4:200	H_2:400,Ar:600	1	10
56	Methane	H_2,Ar	850-1000(900)	CH_4:1000	H_2:100,Ar:100	30	30
57	Methane	N_2	750-850(850)	CH_4:120	N_2:240	10	10
58	Methane	H_2,Ar	900	CH_4:1000	H_2:400,Ar:600		30
59	Acetylene	N_2	720	C_2H_2:10	N_2:1166		30
60	Methanol	Ar	1000-1200	CH_4:30-60	Ar:500-833		
61	Methane	N_2	850-1100(1000)	CH_4:100-400	N_2:200		30
62	Methane	H_2	800-1000				
63	Methane	H_2,Ar	900-1100(1000)	CH_4:140	Ar:560	20	10
64	Methane	H_2	600-690	CH_4:50			
65	Acetylene	N_2	600-690(690)	Total 110			30
66	Acetylene	H_2,N_2	700	C_2H_2:10	N_2:200		60
67	Methane	H_2	800-900(800)	CH_4:5	H_2:50	15	20

68	Ethylene	H_2,N_2	900	C_2H_4:20			
69	Methane	Ar	900	CH_4:16.7	Ar:33.3	10	15
70	Methane	Ar	850	CH_4: 60	Ar: 250		30
71	Ethylene	H_2,Ar	750	C_2H_4:50-400(225)	H_2:40-150(95),Ar:100-300(200)	950	30
72	Acetylene	N_2	700	C_2H_2:45	N_2:592	30	20
73	Acetylene	H_2,Ar	450-850	C_2H_2:42	Ar~368		
74	Ethylene	H_2,Ar	750	C_2H_4:10	H_2:400,Ar:600		5
75	Methane	Ar	900-1100	CH_4:140	Ar:560	20	10
76	Acetylene	Ar	700	C_2H_2:30	Ar:100	20	15
77	Methane	H_2,N_2	500-700(700)	CH_4:60	N_2:420		60
78	Acetylene	NH_3	700-900(700)	C_2H_2:50	NH_3:150	3	5
79	Methane	H_2	690-740(700)	CH_4:900	H_2:50	15	30
80	Acetylene	N_2	750	C_2H_2:100	N_2:500	1	15
81	Methane	H_2,Ar	650-750(1000)	CH_4:80	H_2:800,Ar:200	2	15
82	Acetylene	H_2	600	C_2H_2:1	H_2:9		
83	Methane	N_2	900	CH_4:1000			
84	Ethylene	H_2,Ar	750-950(750)	C_2H_4:20-50(40)	H_2:400,Ar:600	2300	45
85	Acetylene	H_2	800	C_2H_4:10-50	H_2:100		30
86	Acetylene	H_2,Ar	750-900(750)	C_2H_2:12	H_2:100,Ar:600	700	15
87	Acetylene	N_2	750	C_2H_2:100	N_2:300		20
88	Acetylene	H_2,N_2	400-700(700)	C_2H_2:50	H_2:300,N_2:500		
89	Acetylene	H_2,N_2	450	C_2H_2:70	H_2:140,N_2:90	1	60
90	Acetylene	H_2,N_2	650	C_2H_2:60	H_2:120,N_2:160		60

91	Acetylene	H_2,N_2	650	C_2H_2:405	H_2:1200,N_2:685	13	120
92	Acetylene	H_2,N_2	650	C_2H_2:11300	H_2:3800,N_2:6500		120
93	Methane	Ar	1000	CH_4:6150		10	10
94	Acetylene	N_2	720	C_2H_2:10	N_2:1167		30
95	Methane	Ar	900-1000(900)	CH_4:1500	Ar: 60		15
96	Acetylene	H_2,N_2,Ar	750	C_2H_2:9.6	H_2:50,N_2:60	25	60
97	Ethylene	H_2,Ar	750	C_2H_4:100	H_2:500,Ar:200	40-70	1.5
98	Acetylene	H_2	700	C_2H_2:40	H_2: 300	5	30
99	Acetylene		750-900(800)	C_2H_2:20		6	15
100	Acetylene		700	C_2H_2:70		15	30
101	Acetylene		850	C_2H_2:2		1-6	10
102	Acetylene	H_2,Ar	700	C_2H_2:60	H_2:80,Ar:660	60	15
103	Acetylene	H_2,Ar	475	C_2H_2:20	H_2:100,Ar:880	1	15
104	Acetylene	H_2,Ar	500	C_2H_2:20	H_2:100,Ar:880	2	15
105	Acetylene	H_2,Ar	550	C_2H_2:20	H_2:100,Ar:880	9	15
106	Acetylene	H_2,Ar	600	C_2H_2:20	H_2:100,Ar:880	20	15
107	Acetylene	H_2,Ar	650	C_2H_2:20	H_2:100,Ar:880	45	15
108	Acetylene	H_2,Ar	700	C_2H_2:20	H_2:100,Ar:880	25	15

Appendix B

Table 10: Calculations for successful conditions[68-163, 184-188]

	Carbon Source	Temperature (℃)	Q_c(sccm)	Q_h(sccm)	Q_t(sccm)	V(cm3)	Residence Time(min)	Growth rate (um/min)	C_c(mol/cm3)	C_h (mol/cm3)	C_h/C_c	Growth Rate (um/min)
2	ethylene	750.00	100.00	400.00	1100.00	192.96	0.18	250.00	1.08E-06	4.32897E-06	4.00	
4	ethylene	750.00	100.00		1100.00	154.37	0.14	140.00	1.08E-06			140.00
6	ethylene	750.00	100.00	400.00	1100.00	192.96	0.18	250.00	1.08E-06	4.32897E-06	4.00	
7	ethylene	750.00	100.00	400.00	1100.00	192.96	0.18	100.00	1.08E-06	4.32897E-06	4.00	
8	ethylene	750.00	100.00	500.00	800.00	113.98	0.14	66.67	1.49E-06	7.44042E-06	5.00	66.67
12	ethylene	750.00	100.00	500.00	800.00	113.98	0.14	66.67	1.49E-06	7.44042E-06	5.00	66.67
14	ethylene	750.00	100.00	400.00	600.00	113.98	0.19	75.00	1.98E-06	7.93645E-06	4.00	75.00
18	ethylene	750.00	100.00		1000.00	154.37	0.15		1.19E-06			
19	ethylene	775.00	100.00	400.00	600.00	113.98	0.19	100.00	1.94E-06	7.74715E-06	4.00	100.00
20	ethylene	800.00	110.00	400.00	585.00	113.98	0.19	18.00	2.13E-06	7.76069E-06	3.64	
21	ethylene	775.00	100.00	400.00	600.00	113.98	0.19	100.00	1.94E-06	7.74715E-06	4.00	100.00
22	ethylene	775.00	100.00	400.00	600.00	113.98	0.19	100.00	1.94E-06	7.74715E-06	4.00	100.00
23	ethylene	775.00	100.00	400.00	600.00	113.98	0.19	100.00	1.94E-06	7.74715E-06	4.00	100.00
24	acetylene	700.00	16.67		1183.34	1531.32	1.29	33.30	1.76E-07			
29	acetylene	750.00	225.00	95.00	520.00	1531.32	2.94	31.67	5.15E-06	2.17489E-06	0.42	31.67
33	acetylene	750.00	100.00	80.00	260.00	1531.32	5.89	45.00	4.58E-06	3.66298E-06	0.80	45.00
36	methane	1000.00	6150.00		6150.00	154.37	0.025	1.00	9.57E-06			1.00
37	methane	1000.00	3500.00		3500.00	154.37	0.044	2.00	9.57E-06			2.00
38	ethylene	700.00	1000.00		1000.00	617.46	0.62	0.67	1.25E-05			0.67
40	methane	900.00	6000.00		6000.00	154.37	0.026	1.00	1.04E-05			1.00
41	methane	900.00	750.00		750.00	154.37	0.206	0.30	1.04E-05			0.30

42	methane	900.00	500.00		500.00	154.37	0.309	1.00	1.04E-05			1.00
43	methane	900.00	200.00	200.00	400.00	154.37	0.386	0.46	5.19E-06	5.19127E-06	1.00	0.46
44	methane	900.00	1500.00	125.00	1625.00	9879.43	6.080	1.43	9.58E-06	7.98656E-07	0.08	
46	methane	900.00	200.00	200.00	400.00	154.37	0.386	0.46	5.19E-06	5.19127E-06	1.00	0.46
48	methane	800.00	720.00	500.00	1220.00	154.37	0.127	1.50	6.70E-06	4.65165E-06	0.69	1.50
49	methane	900.00	1000.00	500.00	1500.00	154.37	0.103	10.00	6.92E-06	3.46084E-06	0.50	10.00
50	methane	600.00	48.00		60.00	15436.61	257.277	0.10	1.12E-05			
51	methane	720.00	160.00	30.00	192.40	9879.43	51.348	1.00	1.02E-05	1.91231E-06	0.19	1.00
52	methane	700.00	1000.00	500.00	1500.00	1.96	0.001	1.00	8.34E-06	4.17211E-06	0.50	1.00
54	methane	800.00	30.00	440.00	470.00	149.54	0.318	1.50	7.24E-07	1.06255E-05	14.67	
55	ethylene	800.00	200.00	400.00	1200.00			0.10	1.89E-06	3.78334E-06	2.00	1.00
56	methane	900.00	1000.00	100.00	1200.00			1.00	8.65E-06	8.65211E-07	0.10	1.00
57	methane	850.00	120.00		360.00	861.36	2.393	1.00	3.61E-06			
58	methane	900.00	1000.00	400.00	2000.00				5.19E-06	2.07651E-06	0.40	
59	acetylene	720.00	10.00		1176.00	22.61	0.02		1.04E-07			
61	methane	1000.00	250.00		450.00	149.54	0.332		5.32E-06			
63	methane	1000.00	140.00		700.00	382.83	0.547	2.00	1.91E-06			2.00
66	acetylene	700.00	10.00		210.00				5.96E-07			
67	methane	800.00	5.00	50.00	55.00	622.34	11.315	0.75	1.03E-06	1.03182E-05	10.00	0.75
68	ethylene	900.00	20.00	500.00	520.00				3.99E-07	9.9832E-06	25.00	
69	methane	900.00	16.70		50.00	154.37	3.087	0.67	3.47E-06			0.67
70	methane	850.00	60.00		310.00				2.10E-06			
71	ethylene	750.00	225.00	95.00	520.00	1531.32	2.94	31.67	5.15E-06	2.17489E-06	0.42	
72	acetylene	700.00	45.00		637.00			2.00	8.84E-07			2.00
74	ethylene	750.00	10.00	400.00	1010.00	861.36	0.85		1.18E-07	4.71472E-06	40.00	
75	methane	1000.00	140.00		700.00	382.83	0.547	2.00	1.91E-06			2.00
76	acetylene	700.00	30.00		130.00			1.33	2.89E-06			1.33
77	methane	700.00	60.00		480.00				1.56E-06			

78	acetylene	700.00	50.00	150.00	200.00	382.83	1.91	0.60	3.13E-06	9.38725E-06	3.00	0.60
79	methane	700.00	900.00	50.00	950.00			0.50	1.19E-05	6.58754E-07	0.06	0.50
80	acetylene	750.00	100.00		600.00			0.07	1.98E-06			0.07
81	methane	1000.00	80.00	800.00	1080.00			0.13	7.09E-07	7.08669E-06	10.00	
82	acetylene	600.00	1.00	9.00	10.00	157.00	15.70		1.39E-06	1.25548E-05	9.00	
83	methane	900.00	1000.00		1000.00				1.04E-05			
84	ethylene	750.00	40.00	400.00	1040.00	154.37	0.15	51.11	4.58E-07	4.57872E-06	10.00	51.11
85	acetylene	800.00	60.00	100.00	160.00	1345.88	8.41		4.26E-06	7.09376E-06	1.67	
86	acetylene	750.00	12.00	100.00	712.00			46.67	2.01E-07	1.672E-06	8.33	46.67
87	acetylene	750.00	100.00		400.00				2.98E-06			
89	acetylene	450.00	70.00	140.00	300.00			0.02	3.93E-06	7.86023E-06	2.00	
90	acetylene	650.00	60.00	120.00	340.00	98.13	0.29		2.33E-06	4.65679E-06	2.00	
91	acetylene	650.00	405.00	1200.00	2290.00	598.17	0.26	0.11	2.33E-06	6.91402E-06	2.96	0.11
92	acetylene	650.00	11300.00	3800.00	21600.00	24501.04	1.13		6.90E-06	2.32121E-06	0.34	
94	acetylene	720.00	10.00		1177.00	50.87	0.04		1.04E-07			
95	methane	900.00	1500.00		1560.00	314.00	0.201		9.98E-06		0.00	
96	acetylene	750.00	9.60	50.40	120.00			0.42	9.52E-07	4.99996E-06	5.25	0.42
97	ethylene	750.00	100.00	500.00	800.00	113.98	0.14	36.67	1.49E-06	7.44042E-06	5.00	36.67
98	acetylene	700.00	40.00	300.00	340.00	382.83	1.13	0.17	1.47E-06	1.10438E-05	7.50	0.17
99	acetylene	800.00	20.00		20.00			0.38	1.14E-05			
100	acetylene	700.00	70.00		70.00	215.34	3.08	0.50	1.25E-05			0.50
101	acetylene	850.00	2.00		2.00	215.34	107.67	0.35	1.08E-05			
102	acetylene	700.00	60.00	80.00	800.00			4.00	9.39E-07	1.25163E-06		4.00
107	acetylene	650.00	20.00	100.00	1000.00	154.37	0.15	3.00	2.64E-07	1.31942E-06	5.00	3.00
93	methane	1000.00	6150.00		6150.00			1.00	9.57E-06			

Table 11: Calculations for unsuccessful conditions[68-163, 184-188]

	Carbon Source	Temperature (℃)	Q_c(sccm)	Q_h(sccm)	Q_t(sccm)	V(cm3)	Residence Time(min)	Growth rate (um/min)	C_c(mol/cm3)	C_h (mol/cm3)	C_h/C_c
18	ethylene	775.00	100.00		1000.00	154.37	0.15		1.16E-06	0	0.00
18	ethylene	800.00	100.00		1000.00	154.37	0.15		1.14E-06	0	0.00
24	acetylene	720.00	16.67	0.00	1183.34	1531.32	1.29	33.30	1.73E-07	0	0.00
24	acetylene	740.00	16.67	0.00	1183.34	1531.32	1.29	33.30	1.69E-07	0	0.00
52	methane	600.00	1000.00	500.00	1500.00	1.96	0.00	1.00	9.30E-06	4.64993E-06	0.50
52	methane	800.00	1000.00	500.00	1500.00	1.96	0.00	1.00	7.57E-06	3.78334E-06	0.50
54	methane	900.00	30.00	440.00	470.00	149.54	0.32	1.50	6.63E-07	9.71982E-06	14.67
55	ethylene	900.00	200.00	400.00	1200.00			0.10	1.73E-06	3.46084E-06	2.00
55	ethylene	1000.00	200.00	400.00	1200.00			0.10	1.59E-06	3.18901E-06	2.00
56	methane	850.00	1000.00	100.00	1200.00			1.00	9.04E-06	9.03728E-07	0.10
56	methane	950.00	1000.00	100.00	1200.00			1.00	8.30E-06	8.29843E-07	0.10
56	methane	1000.00	1000.00	100.00	1200.00			1.00	7.97E-06	7.97253E-07	0.10
57	methane	750.00	120.00	0.00	360.00	861.36	2.39	1.00	3.97E-06	0	0.00
57	methane	800.00	120.00	0.00	360.00	861.36	2.39	1.00	3.78E-06	0	0.00
61	methane	850.00	250.00	0.00	450.00	149.54	0.33	0.00	6.02E-06	0	0.00
61	methane	900.00	250.00	0.00	450.00	149.54	0.33	0.00	5.77E-06	0	0.00
61	methane	950.00	250.00	0.00	450.00	149.54	0.33	0.00	5.53E-06	0	0.00
61	methane	1050.00	250.00	0.00	450.00	149.54	0.33	0.00	5.11E-06	0	0.00
61	methane	1100.00	250.00	0.00	450.00	149.54	0.33	0.00	4.93E-06	0	0.00
63	methane	900.00	140.00	0.00	700.00	382.83	0.55	2.00	2.08E-06	0	0.00
63	methane	1100.00	140.00	0.00	700.00	382.83	0.55	2.00	1.77E-06	0	0.00
67	methane	850.00	5.00	50.00	55.00	622.34	11.32	0.75	9.86E-07	9.85885E-06	10.00

67	methane	900.00	5.00	50.00	55.00	622.34	11.32	0.75	9.44E-07	9.43867E-06	10.00
75	methane	900.00	140.00	0.00	700.00	382.83	0.55	2.00	2.08E-06	0	0.00
75	methane	1100.00	140.00	0.00	700.00	382.83	0.55	2.00	1.77E-06	0	0.00
77	methane	500.00	60.00	0.00	480.00			0.00	1.97E-06	0	0.00
77	methane	600.00	60.00	0.00	480.00			0.00	1.74E-06	0	0.00
78	acetylene	800.00	50.00	150.00	200.00	382.83	1.91	0.60	2.84E-06	8.51251E-06	3.00
78	acetylene	900.00	50.00	150.00	200.00	382.83	1.91	0.60	2.60E-06	7.7869E-06	3.00
79	methane	690.00	900.00	50.00	950.00			0.50	1.20E-05	6.65594E-07	0.06
79	methane	710.00	900.00	50.00	950.00			0.50	1.17E-05	6.52054E-07	0.06
79	methane	720.00	900.00	50.00	950.00			0.50	1.16E-05	6.45488E-07	0.06
79	methane	730.00	900.00	50.00	950.00			0.50	1.15E-05	6.39054E-07	0.06
79	methane	740.00	900.00	50.00	950.00			0.50	1.14E-05	6.32746E-07	0.06
81	methane	600.00	80.00	800.00	1080.00			0.13	1.03E-06	1.03332E-05	10.00
81	methane	700.00	80.00	800.00	1080.00			0.13	9.27E-07	9.27136E-06	10.00
81	methane	800.00	80.00	800.00	1080.00			0.13	8.41E-07	8.40742E-06	10.00
81	methane	900.00	80.00	800.00	1080.00			0.13	7.69E-07	7.69076E-06	10.00
84	ethylene	800.00	40.00	400.00	1040.00	154.37	0.15	51.11	4.37E-07	4.36539E-06	10.00
84	ethylene	850.00	40.00	400.00	1040.00	154.37	0.15	51.11	4.17E-07	4.17105E-06	10.00
84	ethylene	900.00	40.00	400.00	1040.00	154.37	0.15	51.11	3.99E-07	3.99328E-06	10.00
84	ethylene	950.00	40.00	400.00	1040.00	154.37	0.15	51.11	3.83E-07	3.83004E-06	10.00
86	acetylene	800.00	12.00	100.00	712.00			46.67	1.91E-07	1.5941E-06	8.33
86	acetylene	850.00	12.00	100.00	712.00			46.67	1.83E-07	1.52314E-06	8.33
86	acetylene	900.00	12.00	100.00	712.00			46.67	1.75E-07	1.45822E-06	8.33
95	methane	950.00	1500.00	0.00	1560.00	314.00	0.20		9.58E-06	0	0.00
95	methane	1000.00	1500.00	0.00	1560.00	314.00	0.20		9.20E-06	0	0.00
103	acetylene	475.00	20.00	100.00	1000.00			0.07	3.26E-07	1.62805E-06	5.00
104	acetylene	500.00	20.00	100.00	1000.00			0.13	3.15E-07	1.57541E-06	5.00
105	acetylene	550.00	20.00	100.00	1000.00			0.60	2.96E-07	1.47971E-06	5.00

106	acetylene	600.00	20.00	100.00	1000.00			1.33	2.79E-07	1.39498E-06	5.00
108	acetylene	700.00	20.00	100.00	1000.00			1.67	2.50E-07	1.25163E-06	5.00

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